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**Determination of arsenic in water
using solid-phase extraction disk**

固相抽出ディスクを用いた水中ヒ素の定量

学位請求者 応用化学専攻

萩 原 健 太

Determination of arsenic in water using solid-phase extraction disk

Kenta Hagiwara

Department of Applied Chemistry, Meiji University, Kawasaki 214-8571, Kanagawa, Japan

Abstract

Rapid and simple methods combining disk solid-phase extraction (SPE) with several detection techniques were developed for the determination of As in water.

A method of graphite furnace atomic absorption spectrometry (GFAAS) after disk SPE was developed for the determination of diphenylarsinic acid (DPAA), phenylarsonic acid (PAA), and inorganic As in water. A 200 mL aqueous sample (pH3) was passed through the SPE disks to concentrate DPAA on the Empore SDB-XD disk, PAA on the activated carbon disk, and inorganic As on the Cation-SR disk loaded with Zr and Ca (ZrCa-CED). The As compounds were eluted from the disks, and then analyzed by GFAAS. The detection limits were 0.13–0.16 $\mu\text{g L}^{-1}$. Spike tests of As in drinking water showed good recoveries.

A method of wavelength dispersive X-ray fluorescence (XRF) spectrometry after on-site disk SPE was developed for the speciation of inorganic As in water. A 50 mL aqueous sample (pH 2–3) added with ammonium pyrrolidine dithiocarbamate solution was passed through a PTFE filter placed on a ZrCa-CED to separate As(III) and As(V). Each SPE disk was affixed to an acrylic plate, and then examined by wavelength dispersive XRF spectrometry. The detection limits were 0.6–0.8 $\mu\text{g L}^{-1}$. The proposed method was successfully applied to screening for As speciation in drinking water.

A method using SPE disk and mobile XRF spectrometer was developed for As determination in water. A 50 mL aqueous sample (pH 3) was passed through a Ti and Zr-loaded carbon disk (TiZr-CD) to preconcentrate As. The SPE disk was adhered to an acrylic plate, and then examined by mobile XRF spectrometry. The detection limit was 2.0 $\mu\text{g L}^{-1}$. The As concentrations in well water samples were determined using the proposed method were similar to results obtained from GFAAS. The proposed method did not require a power supply or toxic agents in any analytical step, therefore it is suitable for the on-site determination of As in water.

Keywords: Arsenic; solid-phase extraction disk; drinking water; atomic absorption spectrometry; X-ray fluorescence spectrometry

*All inquiries should be addressed to:

Professor M. Aizawa, Department of Applied Chemistry, Meiji University, 1-1-1 Higashimita, Tama-ku, Kawasaki 214-8571, Kanagawa, Japan.

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Chapter 1 Introduction

1.1 Arsenic pollution and arsenic species in water

Arsenic is one of the most toxic elements found in water derived from various environmental sources. As species found in environmental water are shown in Fig. 1. Ground water mainly contains inorganic arsenite (As(III)) and/or arsenate (As(V)) ions, which are dissolved from soils and minerals, and the distribution of As(III)/As(V) fluctuates widely according to environmental conditions. Naturally occurring inorganic As pollutions ($\mu\text{g L}^{-1}$ – mg L^{-1}) in ground water were found in many countries such as Bangladesh, India, Taiwan, Vietnam, and Argentina [1]. Although fewer cases are reported, organic As, such as methylarsonic acid (MAA), dimethylarsinic acid (DMAA), phenylarsonic acid (PAA), and diphenylarsinic acid (DPAA) appear in drinking water [2, 3] because of microbial activity or human actions. Aromatic As compounds (*e.g.*, *p*-arsanilic acid (*p*-AA) and roxarsone (Rox)) are currently used as feed additives for poultry and swine, and there is a possibility that these As compounds could permeate into ground water [4]. Because pollution of drinking water is common in the world, the World Health Organization (WHO) has recommended an As limit of $10 \mu\text{g L}^{-1}$ for drinking water. Therefore, it is important to monitor As concentration in drinking water supplies.

1.2 Analytical methods of arsenic in water

Sensitive element analysis methods using instrumental techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), graphite furnace atomic absorption spectrometry (GFAAS), and hydride generation atomic absorption spectrometry (HGAAS) have been used for the determination of total As in water [5].

The toxicity levels of As depends on its chemical form due to differences in the mechanisms of action. For example, As(III) is more toxic than As(V) [6], and inorganic arsenic is more toxic than organic arsenic [7, 8]. Therefore, the speciation of As is required when evaluating the toxicity of water samples. Analytical methods that involve the coupling of separation techniques, such as high performance liquid chromatography (HPLC) [9–11], solid-phase extraction (SPE) [12, 13], and liquid-liquid extraction (LLE) [14, 15] with above sensitive detection techniques, have been used for the speciation of As in water.

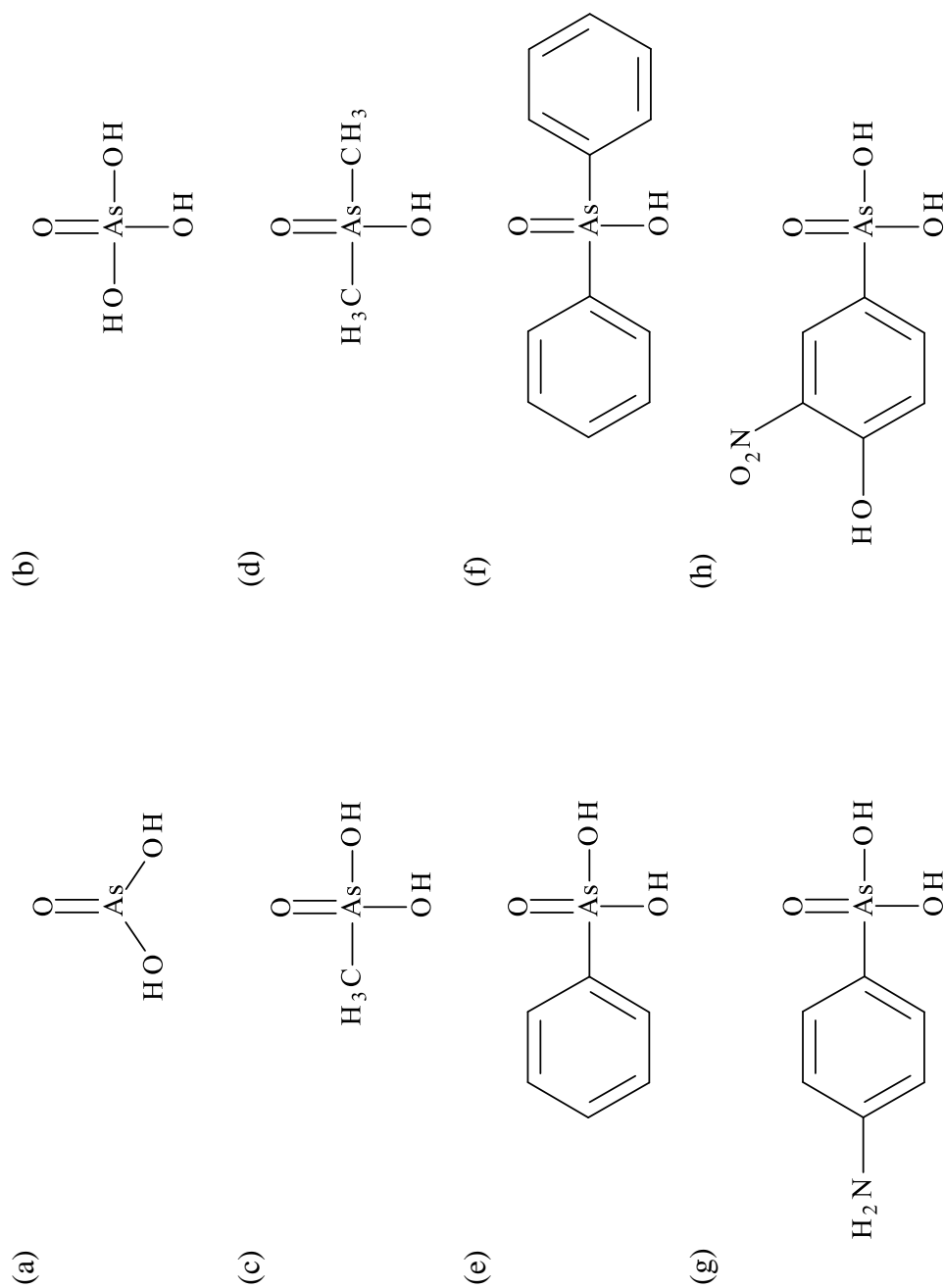


Fig. 1 As species found in water. (a): Arsenite, (b): arsenate, (c): methylarsenite, (d): dimethylarsenite, (e): phenylarsenite, (f): diphenylarsenite, (g): *p*-arsanilic acid, and (h): roxarsone.

1.3 Solid-phase extraction disk

SPE has been widely used in pharmaceutical, industrial, and environmental fields to separate and/or preconcentrate inorganic and organic analytes. In particular, membrane disk SPEs have been used to pretreat large volume water samples because they allow relatively high flow rates, due to their large cross sectional areas [16]. SPE disks keep their shape during the pretreatment process to assay, so they are useful for wet analyses [17, 18] as well as direct analyses, *e.g.*, X-ray fluorescence (XRF) spectrometry [19–21], γ -ray spectrometry [22, 23], and laser induced breakdown spectroscopy [24]. An analytical method using an iminodiacetate chelating disk, followed by direct introduction into GFAAS instrument, has also been reported for determining heavy metals at sub $\mu\text{g L}^{-1}$ levels in water [25]. Therefore, SPE disks are adaptable, and can be used for quantitative analyses using various instruments. In addition, multiple SPE disk layers allow for the simultaneous collection of different analytes (*e.g.*, Cr(III) and Cr(VI)) [17, 19] from a water sample.

In this article, rapid and simple methods combining disk SPE with several detection techniques were developed for the determination of As in drinking water.

Chepter 2 Determination of diphenylarsinic acid, phenylarsonic acid and inorganic arsenic in water by disk solid-phase extraction/graphite furnace atomic absorption spectrometry

2.1 Phenylarsenic pollution

Well water polluted with organic As compounds was found at Kamisu town, Ibaraki, Japan, in 2003 [3]. The pollutants were predominantly phenylarsenic compounds: DPAA and PAA, which were considered to be the raw materials or degradation products of sternutatory gases used as chemical warfare agents (CWAs). Large amounts of CWAs were produced and distributed around the world during the first and second world wars. In Japan, many CWAs were abandoned underground, in lakes and in the sea after the wars had ended. The CWAs that are discovered are detoxified by the government [26]. The deterioration of an As containing CWA may cause As pollution in soil and/or environmental water.

2.2 Analytical methods of phenylarsenic spices in water

Phenylarsenic compounds can be derivatized and determined by gas chromatography-mass spectrometry (GC-MS) [27, 28], but this method is tedious and cannot be used to simultaneously detect inorganic As. HPLC-ICP-MS has been used for separate determinations of phenylarsenic compounds and inorganic As in water [29–31]; however, this technique is relatively expensive, and well trained personnel are required. A sensitive analytical method using liquid chromatography mass spectrometry (LC-MS) [32] or liquid chromatography-tandem mass spectrometry (LC-MS-MS) [33] has been developed for the simultaneous determination of phenylarsenic compounds. These methods are useful for the routine analysis of phenylarsenic compounds, but cannot be applied to the ordinary determination of As in water because inorganic As cannot be determined. An analytical method using SPE followed by GFAAS allows the speciation of elements to be determined. It is easy to conduct, has low capital (equipment) cost, and low running costs, although this method cannot be used to simultaneously determine many analytes unlike HPLC-ICP-MS. Several methods combining SPE with GFAAS have been reported for the determination of inorganic As [34–36] and DPAA [37] in water. However, the separation analysis of DPAA, PAA, and inorganic As using SPE and GFAAS has not yet been reported.

In this chapter, a method for determining DPAA, PAA, and inorganic As (As(III) and

As(V)) in drinking water using SPE, followed by GFAAS is described. This method involves the preconcentration of DPAA, PAA, and inorganic As on a polystyrene divinylbenzene disk, an active carbon disk, and a cation exchange extraction disk loaded with Zr and Ca (ZrCa-CED), respectively. The discussion covers: calibration curves; the effect of Zr and Ca on the cation exchange extraction disk; the optimum sample pH, flow rate, eluent concentration and volume; and the influence of coexisting ions. The proposed method was successfully used to determine $\mu\text{g L}^{-1}$ levels of DPAA, PAA, and inorganic As in tap water and natural mineral water.

2.3 Experimental

2.3.1 Apparatus

A ZEE nit 600s atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) fitted with an As hollow cathode lamp (Hitachi, Tokyo, Japan), a transverse heated graphite atomizer, and an SSA 61Z automatic sampling system (Analytik Jena AG) was used. The Zeeman effect was used for background correction under two field mode (0.8 T magnetic field strength) conditions. Atomization was conducted in solid sampling (SS) graphite tubes (Analytik Jena AG, Part No. 407-152.361) with SS graphite platforms (Analytik Jena AG, Part No. 407-152.023). Ten microliters of the sample solution was injected into the SS graphite platform, and 5 μL of a matrix modifier was added to control the analyte atomization process. The operating conditions are given in Table 1.

A RIX3100 wavelength dispersive XRF spectrometer (Rigaku, Tokyo, Japan) was used, with an end window 4 kW Rh X-ray tube operated at 50 kV and 80 mA under vacuum. The irradiation diameter of the primary X-ray beam was 30 mm. A 0.1 mm thickness laminate film (Meiko Shokai, Tokyo, Japan) was used to coat the SPE disk before XRF analysis, to prevent it from being damaged by X-rays [19, 20].

A Demi-Ace Model DX-15 demineralizer (Kurita Water Industries, Tokyo, Japan) was used to prepare deionized water. An F-52 pH meter (Horiba, Kyoto, Japan) was used to monitor the pH of the sample solution.

2.3.2 Reagents and samples

A 10 mg L^{-1} DPAA (99.6%; Wako Pure Chemical Industries, Osaka, Japan) stock solution and a 1000 mg L^{-1} PAA (96%; Wako Pure Chemical Industries) stock solution were prepared in deionized water. A 1000 mg L^{-1} As(III) stock solution (pH 5) was

Table 1 Instrumental conditions for graphite furnace atomic absorption spectrometer for As determination

Apparatus	Analytik jena AG ZEEmit 600s				
Instrumental conditions					
Analytical line / nm	193.7				
Lamp current / mA	8.0				
Slit width / nm	1.2				
Absorbance	Peak area				
Atomization conditions					
Step	Temperature / °C	Ramp / s	Hold / s	Ar gas flow / L min ⁻¹	
Drying 1	90	5	10	2	
Drying 2	105	3	10	2	
Drying 3	110	2	20	2	
Pyrolysis	600	250	45	2	
Atomizing	2500	1100	4	0.2	
Cleaning	2600	500	3	2	

prepared by dissolving arsenic(III) oxide (99%; Junsei Chemical, Tokyo, Japan) in 1 mol L⁻¹ NaOH solution, and then adding 2 mol L⁻¹ HCl and deionized water. A 1000 mg L⁻¹ As(V) stock solution was prepared by dissolving disodium hydrogen arsenate heptahydrate (99%; Junsei Chemical) in deionized water. A 400 mg L⁻¹ Pd matrix modifier solution for the GFAAS determinations was prepared by diluting a Pd solution (analytical reagent grade; Wako Pure Chemical Industries) with 3 mol L⁻¹ HNO₃. A 0.05 mol L⁻¹ Zr solution and a 0.01 mol L⁻¹ Ca solution, for modifying the Cation-SR disks, were prepared by dissolving zirconyl nitrate dihydrate (pure grade; Wako Pure Chemical Industries) and calcium carbonate (guaranteed grade; Junsei Chemical), respectively, in 0.1 mol L⁻¹ HNO₃. All other reagents used were of extrapure grade.

EmporeTM SDB-XD, activated carbon, and Cation-SR disks (47 mm diameter and 0.5 mm thickness; 3M, Saint Paul, USA) were used throughout the study.

A tap water sample and natural mineral water sample were obtained from Kawasaki, Kanagawa, Japan. Water samples were filtered through a GMF-150 glass fiber filter (1.0 µm pore size, 47 mm diameter, 0.73 mm thickness; Whatman, Kent, England) and analyzed immediately using the proposed method.

2.3.3 *Conditioning of solid-phase extraction disks*

SDB-XD and activated carbon disks were conditioned successively with 10 mL of methanol and 10 mL of deionized water. Cation-SR disks were conditioned successively with 10 mL of methanol, 10 mL of deionized water, 20 mL of 3 mol L⁻¹ HNO₃, and 20 mL of deionized water. A ZrCa-CED was then prepared according to the later procedure.

2.2.4 *Preconcentration and determination procedures*

A 200 mL water sample was adjusted to pH 3 with HNO₃, and then passed through the three conditioned SPE disks layered together (*i.e.*, an SDB-XD disk as the upper layer, an activated carbon disk as the middle layer, and a ZrCa-CED as the lower layer) at a flow rate of 15 mL min⁻¹. DPAA was collected by the SDB-XD disk, PAA by the activated carbon disk, and inorganic As by the ZrCa-CED. The disks were washed with 10 mL of deionized water, and then separated for subsequent elution of the As compounds. The collected As compounds were eluted with: 10 mL of ethanol containing 0.5 mol L⁻¹ NH₃ solution to elute DPAA; 20 mL of 1 mol L⁻¹ NH₃ solution to elute PAA; and 20 mL of 6 mol L⁻¹ HCl to elute inorganic As. The eluate of DPAA was diluted to 20 mL with deionized water and the eluates of PAA and inorganic As were diluted to 25 mL with deionized water. The analytes were determined in these sample solutions by GFAAS. The

concentrations of DPAA, PAA, and inorganic As were calculated using a calibration curve previously constructed with a suite of As(V) standard solutions.

2.4 Results and discussion

2.4.1 Calibration curve

Calibration curves for DPAA, PAA, and inorganic As were first constructed with the standard solution of each compound to determine whether the GFAAS instrument gave different sensitivities for these analytes. The calibration curves of DPAA, PAA, As(III), and As(V) showed good linearity in the range of 0.1–2 ng. The linear equations for the calibration curves were as follows: $I = 0.1143M + 0.004115$ ($r = 0.9995$) for DPAA, $I = 0.1149M + 0.006731$ ($r = 0.9991$) for PAA, $I = 0.1153M + 0.005603$ ($r = 0.9991$) for As(III), $I = 0.1155M + 0.004756$ ($r = 0.9997$) for As(V), where M is the absolute amount injected (ng), I is the integrated absorbance, and r is the correlation coefficient. The detection limits, defined as three times the standard deviation ($n = 3$) of the blank values, were 9 pg for PAA and As(III), and 13 pg for DPAA and As(V). The calibration curve slopes for all of the analytes agreed well, and there were no differences in the sensitivities of GFAAS instrument for the between phenylarsenic compounds and the inorganic As, which was probably because the HNO_3 in the matrix modifier solution promoted the decomposition of organic arsenics during the pyrolysis step. Arsenic was determined by comparing the calibration curves in a certified reference material (JSAC 0302-3) with the accuracy of the calibration curves obtained. Furthermore, the concentrations of As obtained ($4.8\text{--}5.2\text{ }\mu\text{g L}^{-1}$) agreed well with the certified value ($5.2\pm0.1\text{ }\mu\text{g L}^{-1}$).

2.4.2 Preparation of solid-phase extraction disks

An Empore Anion-SR (anion exchange extraction) disk will only partially adsorb inorganic As (*ca.* 80%) from tap water [16], although As(III) and As(V) are anions in neutral–alkaline solution. However, a cation exchange silica gel [38] and a cation exchange chelating resin [39], each loaded with Zr, have been shown to be capable of collecting inorganic As quantitatively. Because these solid phases use the complex forming reaction between inorganic As and Zr to collect the As species. However, if a membrane disk SPE is used, some of the inorganic As may pass through the disk because of the short contact time between the inorganic As and the adsorbent. Therefore, the ability of a Zr-loaded cation exchange extraction disk (Zr-CED) to quantitatively adsorb As(III) and As(V) was

investigated. A Zr-CED was prepared by successively passing 20 mL of 0.05 mol L⁻¹ Zr solution and 20 mL of deionized water through a Cation-SR disk. A 60 mL water sample containing 10 µg of As(III) or As(V) was adjusted to pH 3, and then passed through the Zr-CED at a flow rate of 5 mL min⁻¹. The adsorption rate of inorganic As on the SPE disk was calculated from the difference between the As concentrations in the initial solution and the filtrate. The Zr-CED adsorbed As(III) quantitatively (100%), but only adsorbed 10–30% of the As(V). Most of the As(V) passed through the disk; nevertheless, Zr loaded silica gel [38] and resin [39] adsorb As(V) at pH 2–8, as reported in the previous papers. The Zr-CED was then modified with Ca, which inhibits the elution of As from coal fly ash [40] and ordinary Portland cement [41]. The adsorption rate of As(V) with the Zr and Ca modified SPE disk was improved to 100%, which means that the ZrCa-CED completely adsorbed both As(III) and As(V). A ZrCa-CED was analyzed by XRF to confirm that Zr and Ca were loaded onto the Cation-SR disk. As shown in Fig. 2, Zr K α and Ca K α were found in the ZrCa-CED. Therefore, in subsequent extractions, inorganic As was extracted with a ZrCa-CED that was prepared by passing 20 mL of a 0.05 mol L⁻¹ Zr solution, 20 mL of deionized water, 20 mL of a 0.01 mol L⁻¹ Ca solution, and 20 mL of deionized water through a Cation-SR disk.

2.4.3 Sample pH

The pH of an aqueous sample is an important factor in adsorption studies. Therefore, the pH dependence for the adsorption rates of DPAA, PAA, and inorganic As collected on an SDB-XD disk, an activated carbon disk, and a ZrCa-CED was investigated. The pH of the sample solution was controlled using a HNO₃ and NaOH solution. The pH dependences of the adsorption rates for 10 µg of DPAA, PAA, As(III), and As(V) are shown in Fig. 3. DPAA was adsorbed quantitatively, but the other As species were not adsorbed by the SDB-XD disk at pH 2–5, so SDB-XD disks can be used to separate DPAA from other As species at pH 2–5. PAA was adsorbed quantitatively by the activated carbon disk at pH 2–7, and As(V) was adsorbed quantitatively by the activated carbon disk at pH 4–7, but not adsorbed at pH 2–3. As(III) was not adsorbed by the activated carbon disk at pH 2–7. Therefore, activated carbon disks can be used to separate PAA from inorganic As at pH 2–3. The ZrCa-CED adsorbed As(III) and As(V) quantitatively at pH 3–7 and 2–7, respectively. Therefore, a sample solution pH of 3 was chosen to separate DPAA, PAA, and inorganic As in water.

A π – π interaction mechanism is considered to be responsible for the adsorption of phenylarsenic compounds by hydrophobic SPE disks. However, PAA was not adsorbed by

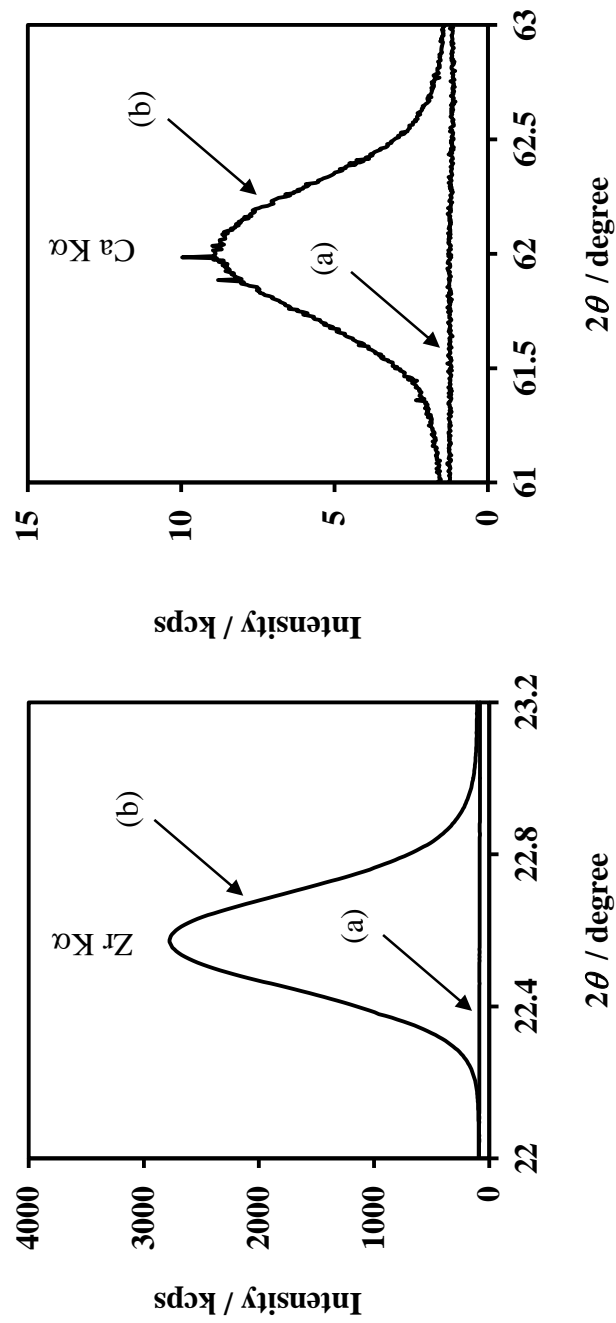


Fig. 2 XRF spectra of Zr K α and Ca K α for (a) a Cation-SR disk and (b) a ZrCa-CED.

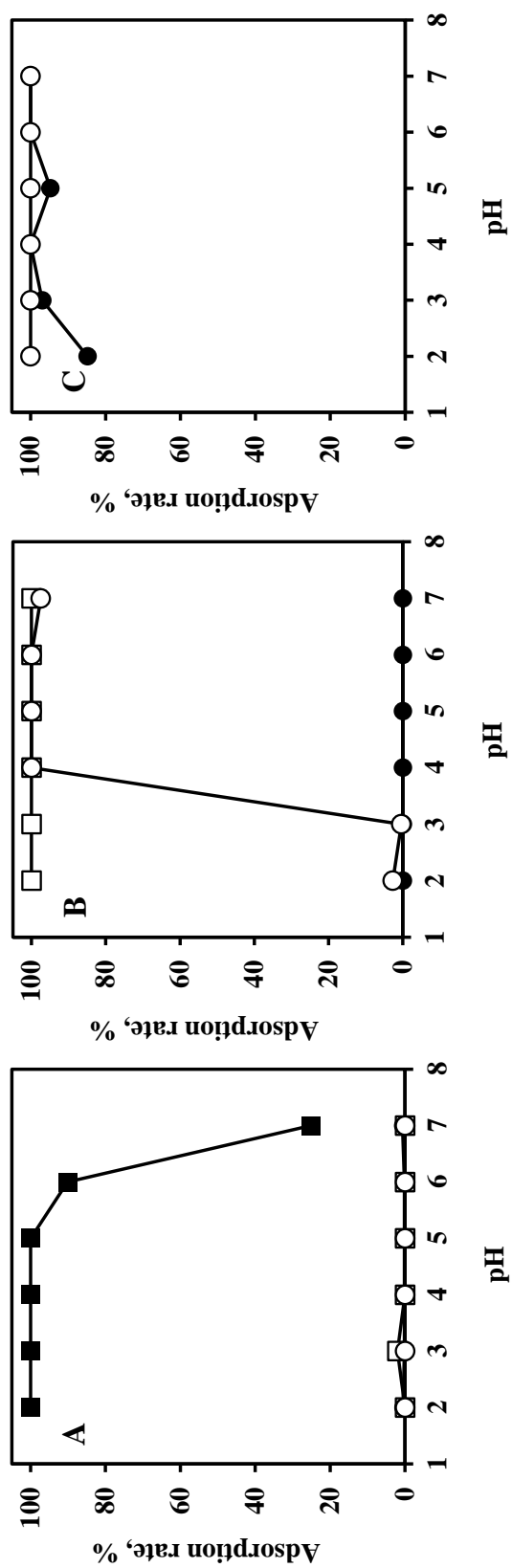


Fig. 3 Adsorption rates of DPAA (■), PAA (□), and iAs (As(III), ●; As(V), ○) at different pH values on (A) an SDB-XD disk, (B) an activated carbon disk, and (C) a ZrCa-CED.

the SDB-XD disk in this study, suggesting that there were no interactions between the phenyl group of PAA and the benzene rings of SDB-XD. PAA may be relatively hydrophilic because it has two hydroxyl groups, but nonetheless PAA was adsorbed by the activated carbon disk, which is a hydrophobic SPE disk. This is probably because of polar interactions (*e.g.*, between arsenate group of PAA and acid functionalities of activated carbon disk), such as hydrogen bonds and dipolar coupling besides π - π interactions.

2.4.4 Sample flow rate

It is expected that the likelihood of DPAA, PAA and inorganic As passing through the solid phase without adsorption would increase with sample solution flow rate. Therefore, the influence of the flow rate on the adsorption rates of the analytes was investigated (Fig. 4). DPAA, PAA, and As(III) were quantitatively adsorbed at flow rates of 5–20 mL min⁻¹, but the adsorption rate of As(V) was insufficient when the flow rate was above 15 mL min⁻¹. Therefore, a sample flow rate of 15 mL min⁻¹ or lower is required to collect the analytes using the three chosen SPE disks.

2.4.5 Eluent and its concentration

The chemical species in the eluent and its concentration are important parameters in the desorption step. Organic compounds collected on a polar phase are usually eluted with an alcohol (being an organic solvent) with or without an NH₃ solution. Therefore, a mixture of ethanol and NH₃ solution was used to elute DPAA. However, an NH₃ solution diluted with deionized water was used to elute PAA, because PAA is more hydrophilic than DPAA. HCl [12, 38, 42] and a NaOH solution [38, 39] have till until now been used to elute inorganic As from Zr adsorbents. However, if a NaOH solution was used, it would be released during the GFAAS drying step, and interfere with the atomization of the inorganic As. Therefore, HCl was selected to elute inorganic As.

Figure 5 shows the recoveries of DPAA, PAA, and inorganic As at different eluent concentrations. The best recoveries of DPAA and PAA were obtained at NH₃ concentrations higher than 0.5 mol L⁻¹ and 1 mol L⁻¹, respectively; 6 mol L⁻¹ HCl eluted both As(III) and As(V) perfectly. From these results, ethanol containing a 0.5 mol L⁻¹ NH₃ solution, a 1 mol L⁻¹ NH₃ solution, and 6 mol L⁻¹ HCl as the eluents for DPAA, PAA, and inorganic As, respectively, were chosen.

The effect of using different eluent volumes (Fig. 6) on the recoveries of the As compounds was investigated to estimate the possible enrichment factors. Ten micrograms of DPAA and PAA were completely eluted using 10 mL of ethanol containing a 0.5 mol L⁻¹

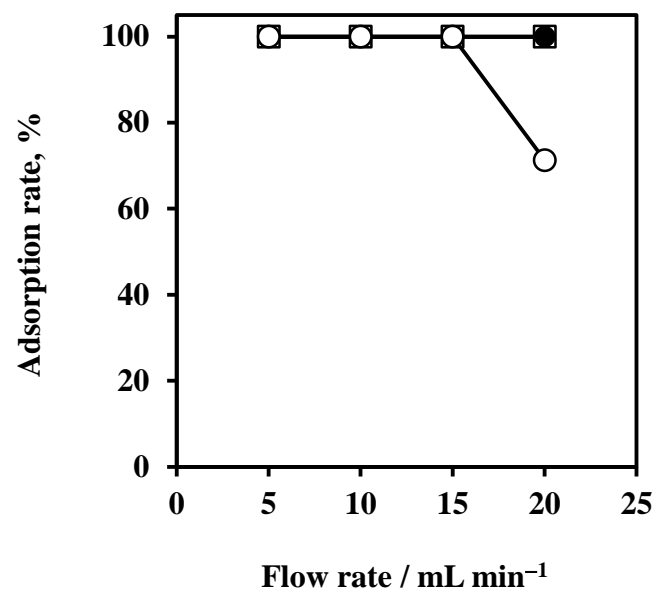


Fig. 4 Adsorption rates of DPAA (■), PAA (□), and iAs (As(III), ●; As(V), ○) at different solution flow rates on an SDB-XD disk, an activated carbon disk, and a ZrCa-CED, respectively.

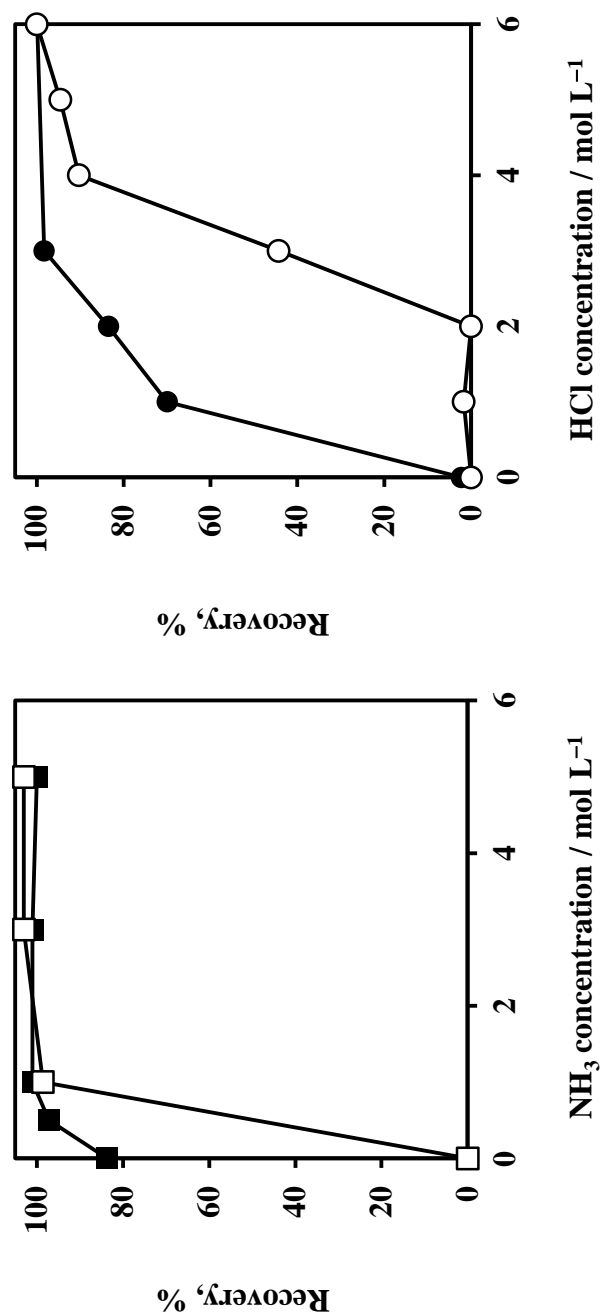


Fig. 5 Recoveries of DPAA (■), PAA (□), and iAs (As(III), ●; As(V), ○) at different NH_3 or HCl concentrations in the eluent using an SDB-XD disk, an activated carbon disk, and a ZrCa-CED, respectively.

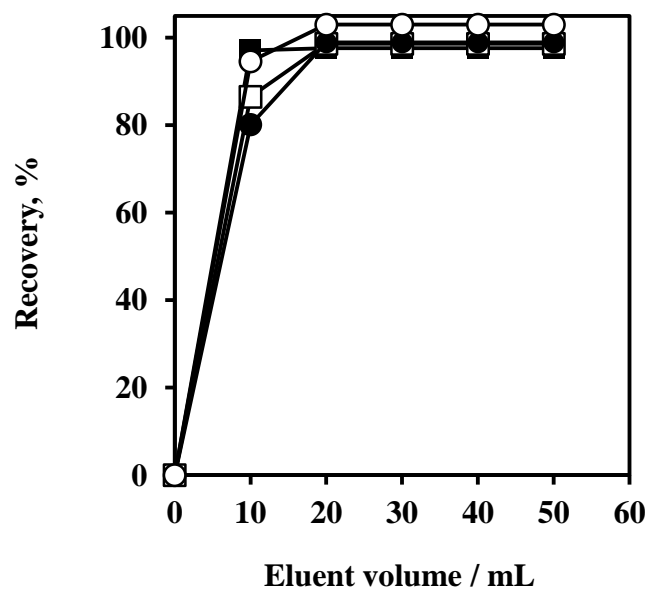


Fig. 6 Recoveries of DPAA (■), PAA (□), and iAs (As(III), ●; As (V), ○) at different eluent volumes using an SDB-XD disk, an activated carbon disk, and a ZrCa-CED, respectively.

NH₃ solution and 20 mL of a 1 mol L⁻¹ NH₃ solution, respectively. Furthermore, 20 mL of 6 mol L⁻¹ HCl perfectly eluted both As(III) and As(V). Therefore, an enrichment factor of 8–10 was achieved when extracting a 200 mL water sample, which gave As detection limits of 0.13–0.16 µg L⁻¹ in the original sample. These detection limits are lower than the maximum value of As (10 µg L⁻¹) established by the WHO for drinking water.

2.4.6 Influence of coexisting ions

Coexisting ions in a water sample may decrease the recoveries of DPAA, PAA, and inorganic As during the preconcentration step. The major ions present in the Tamagawa River were selected as coexisting ions [43] for the tests. When 2.0 µg (10 µg L⁻¹) of DPAA, PAA, and As(V) (as the inorganic As) each were added to 200 mL of artificial freshwater containing 5 mg L⁻¹ of Na⁺, 3 mg L⁻¹ of K⁺, 5 mg L⁻¹ of Mg²⁺, 50 mg L⁻¹ of Ca²⁺, 10 mg L⁻¹ of Cl⁻, and 20 mg L⁻¹ of SO₄²⁻, the recoveries of DPAA, PAA, and As(V) were 101%, 103%, and 101%, respectively. Therefore, typical concentrations of major ions in freshwater did not interfere with the recoveries of the analytes. Next, the effect of Fe (0.3 mg L⁻¹, the drinking water quality of Fe established by WHO) on the recoveries of arsenic compounds was investigated because it has been reported that Fe affects the adsorption of inorganic As on Zr loaded resin [39]. DPAA and PAA were recovered quantitatively (99.5% and 93.8%, respectively), but the recovery of As(V) was only 60.8%.

2.4.7 Applications

The proposed method was used to determine µg L⁻¹ levels of DPAA, PAA, and inorganic As in tap water and natural mineral water. The accuracies of the DPAA, PAA, and inorganic As concentrations determined were evaluated from spiked water sample tests. The spiked test results are given in Table 2. Good agreement was found between the added and established As species values. The good recoveries found (96.1%–103.8%) indicate that the proposed method will be useful for determining µg L⁻¹ levels of phenylarsenic compounds and inorganic As in water.

Table 2 Spike tests for DPAA, PAA, and inorganic As added to tap water and natural mineral water

Sample	Added / $\mu\text{g L}^{-1}$				Found / $\mu\text{g L}^{-1}$				Recovery, %		
	DPAA	PAA	iAs		DPAA	PAA	iAs		DPAA	PAA	iAs
Tap water	0	0	0		N.D.	N.D.	N.D.		–	–	–
	10.00	10.00	10.00		9.61 (3.9)	10.11 (4.5)	10.16 (4.1)		96.1	101.1	101.6
Natural mineral water	0	0	0		N.D.	N.D.	3.94 (5.0)		–	–	–
	10.00	10.00	10.00		10.38 (2.0)	9.97 (1.3)	13.74 (4.7)		103.8	99.7	98.0

iAs: Inorganic As.

N.D.: Not detected.

(): Relative standard deviation, % ($n = 3$).

Chapter 3 Speciation of inorganic arsenic in water by disk solid-phase extraction/wavelength dispersive X-ray fluorescence spectrometry

3.1 Speciation methods of inorganic arsenic in water

Sensitive analytical methods using chromatographic or extraction separation incorporating various instrumental detection techniques such as HPLC-ICP-MS [9–11], SPE/HGAAS [12, 13], and LLE/GFAAS [14, 15], have been used for the *in lab* speciation of As in water. However, these methods must incorporate a rapid assay to obtain the correct quantitative values because As(III) and As(V) tend to be unstable in natural water depending on the water chemistry [44]. There is a possibility that As(III) and As(V) are adsorbed on suspended matter, and coprecipitated with Fe and Mn hydroxides. Moreover, oxidation–reduction substances in water may cause a change in the chemical form of As(III) and As(V). Some pretreatment techniques to improve the stability of inorganic As species have been reported [44, 45]. However, all these methods require severe thermal management, addition of preservatives, and rapid removal of suspended matter. Naturally, these complications can be avoided by the on-site analysis or the separation of As(III) and As(V) in water.

Stripping voltammetry (SV) [46] and colorimetry [47–50] have been developed for the on-site speciation of inorganic As in water. These methods are applied so easily and inexpensively that they are available not only to analysts but also to the general public. However, SV requires a power supply and As standard solutions for the on-site calibration. Colorimetry can be performs the speciation of As on a scale of $\mu\text{g L}^{-1}$ using densitometer [47] or absorptiometer [48–50] instead of visual inspection. However, this method requires the operation of oxidizing and/or reducing with heating.

SPE is suitable for on-site separation and collection of As species in environmental water because it does not require a power supply and numerous acid–base solutions and/or organic solvents in the sample flow step. An on-site preconcentration method using a column type SPE followed by HGAAS has been developed for the determining As(III) and As(V) in water [38]. This method is simple and useful for sensitive analysis, although the method cannot be applied to the screening of a large number of water samples because the elution step is tedious. In contrast, as a pretreatment before assay, membrane disk SPE agents retain their shape during the pretreatment, and are useful for direct analysis by XRF spectrometry. Several methods combining disk SPE with XRF spectrometry have been

reported for the screening of trace elements in water [18, 19, 21, 52]. However, the separation analysis of As(III) and As(V) using this method has not yet been reported.

In this chapter, a method for determining As(III) and As(V) in drinking water using on-site membrane disk SPE followed by wavelength dispersive XRF spectrometry is described. This method involves the preconcentration of As(III) and As(V) on a hydrophilic polytetrafluoroethylene (PTFE) filter and a Zr and Ca loaded cation exchange extraction disk (ZrCa-CED). The remainder of this study addresses the optimum sample pH and flow rate, the preservation of the SPE disk, calibration curves, the removal of Pb^{2+} from the sample water, and the effect of coexisting ions. The proposed method was successfully used to determine the levels of As(III) and As(V) in drinking water on a scale of $\mu\text{g L}^{-1}$.

3.2 Experimental

3.2.1 Apparatus

A RIX3100 wavelength dispersive XRF spectrometer (Rigaku) with an end window 4 kW Rh X-ray tube operating at 50 kV and 80 mA under vacuum conditions was employed for the analysis. The irradiation diameter of the primary X-ray beam was 20 mm. The instrumental conditions are listed in Table 3.

A ZEE nit 600s graphite furnace atomic absorption spectrometer (Analytik Jena AG) was used for determining As and Pb in the filtrates. The measurements of As were conducted under equivalent conditions, as previous chapter. The measurement conditions for Pb were as follows: analytical line, 283.3 nm; drying step, 90°C–110°C for 72 s; pyrolysis step, 900°C for 13 s; and atomizing step, 2400°C for 4 s.

A Demi-Ace Model DX-15 demineralizer (Kurita Water Industries) was used to prepare deionized water. An F-52 pH meter (Horiba) was used for the pH control of the test solution. A U-52 multi water tester (Horiba) was used to monitor the pH, temperature, and dissolved oxygen of the sample water. An FS-320 electric oven (Advantec, Tokyo, Japan) was used for drying the SPE disks.

3.2.2 Reagents

A 1000 mg L^{-1} As(III) stock solution (pH 5) was prepared by dissolving arsenic(III) oxide (99%; Junsei Chemical) in a 0.1 mol L^{-1} NaOH solution, and then adding 1 mol L^{-1} HCl and deionized water. A 1000 mg L^{-1} As(V) stock solution was prepared by dissolving

Table 3 Instrumental conditions for WDXRF spectrometer for As determination

Apparatus	Rigaku RIX3100
Analytical line	K α
Slit	Coarse
Crystal	LiF(200)
Detector	Scintillation counter
Beam filter	Cu
Peak angle, 2θ / degree	33.98
Counting time / s	100
Background angle, 2θ / degree	33.35, 34.85
Counting time / s	100

disodium hydrogen arsenate heptahydrate (99%; Junsei Chemical) in deionized water. A 1000 mg L⁻¹ Pb stock solution was prepared by dissolving lead nitrate (guaranteed grade; Kanto Chemical, Tokyo, Japan) in deionized water. A 0.05 mol L⁻¹ Zr solution and a 0.01 mol L⁻¹ Ca solution, utilized for modifying the cation exchange disks, were prepared by dissolving zirconyl nitrate dihydrate (guaranteed grade; Junsei Chemical) and calcium nitrate tetrahydrate (guaranteed grade; Wako Pure Chemical Industries), respectively, in 0.1 mol L⁻¹ HNO₃. A 0.06 mol L⁻¹ ammonium pyrrolidine dithiocarbamate (APDC, analytical reagent grade; Wako Pure Chemical Industries) solution was prepared in deionized water. All other reagents used were of extra pure grade.

Iminodiacetate chelating disks and cation exchange disks (EmporeTM Chelating and Cation-SR, respectively; 8.0 nm pore size, 47 mm diameter, and 0.5 mm thickness; 3M) and hydrophilic PTFE membrane filters (0.5 µm pore size, 47 mm diameter, and 35 µm thickness; Advantec) were used. These disks were cut to 13 mm diameter and then washed with 1 mol L⁻¹ HNO₃ before use. The sample and conditioning solutions were passed through the SPE miniature disks by pressurization using a plastic syringe with a filter holder.

3.2.3 *Conditioning of solid-phase extraction disks*

Chelating disks were swollen with methanol and conditioned successively with 2.5 mL of deionized water, 5 mL of a 0.1 mol L⁻¹ CH₃COONH₄ solution, and 2.5 mL of deionized water. Cation exchange disks were swollen with methanol, and then ZrCa-CEDs were prepared by successively passing 2.5 mL of deionized water, 2.5 mL of a 0.05 mol L⁻¹ Zr solution, 2.5 mL of deionized water, 2.5 mL of a 0.01 mol L⁻¹ Ca solution, and 2.5 mL of deionized water through the cation exchange disk.

3.2.4 *On-site preconcentration procedure*

The on-site SPE procedure for the preconcentration and separation of As(III) and As(V) is illustrated in Fig. 7. A 50 mL water sample of pH 5–9 adjusted as needed with HCl or NaOH solution was passed through a chelating disk at a flow rate of 20 mL min⁻¹ for removing Pb²⁺ and suspended matter. As(III) and As(V), which were partially adsorbed on the disk, were eluted with 0.5 mL of a pH 13 NaOH solution, and the eluent was added to the filtrate. The filtrate was adjusted to pH 2–3 with a pH 1 HCl solution. One milliliter of 0.06 mol L⁻¹ APDC solution was added and stirred for 2 min to form the As(III)-PDC complex. This solution was passed through a PTFE filter placed on a ZrCa-CED at a flow rate of 12.5 mL min⁻¹ to separate As(III) and As(V). As(III) was collected by the upper

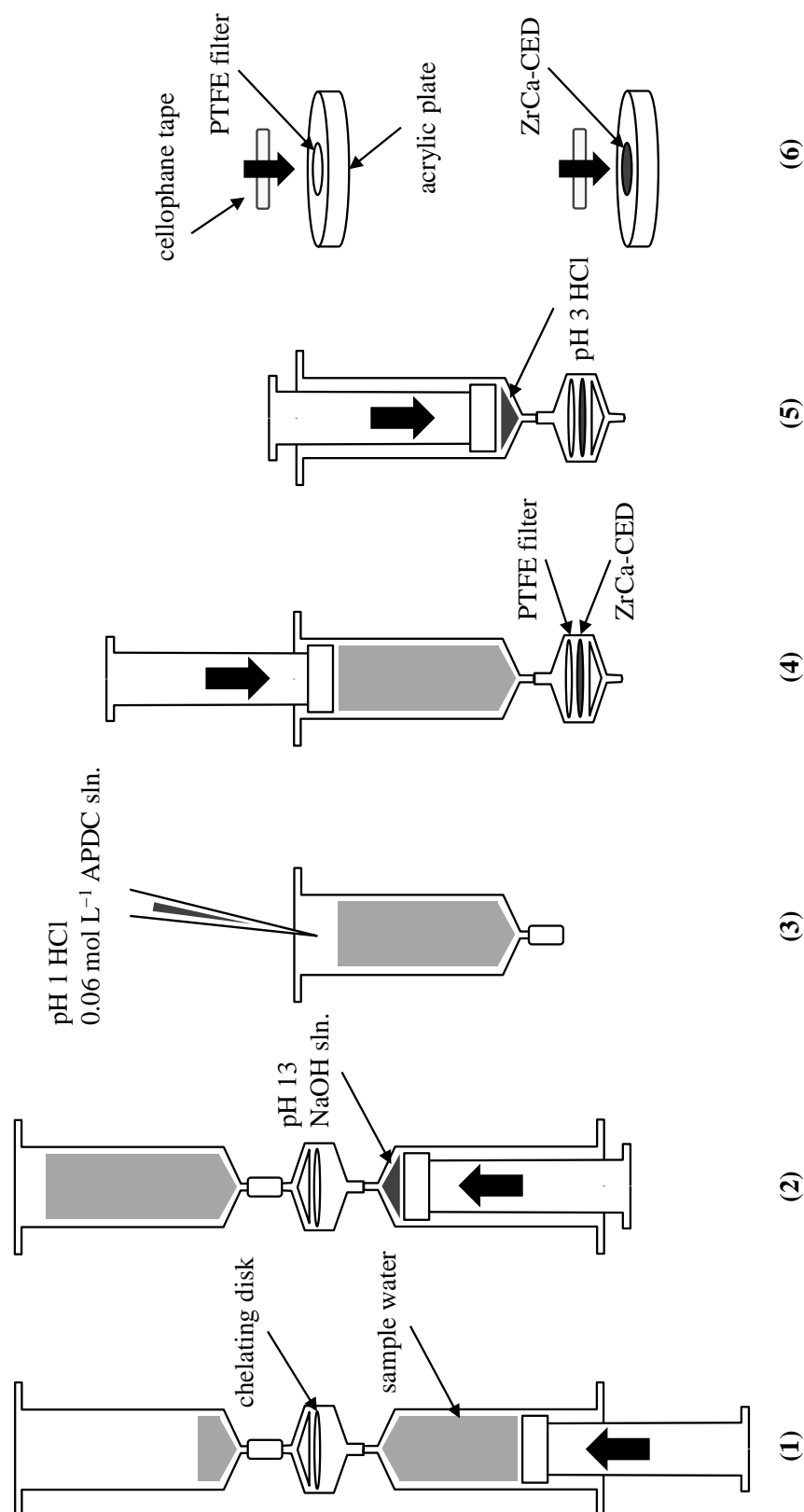


Fig. 7 Proposed process of on-site solid-phase extraction for separation and preconcentration of As(III) and As(V) in water. (1) Removal of Pb^{2+} and suspended matter, (2) elution of analytes, (3) pH adjustment and complex formation, (4) separate collection of As(III) and As(V) on PTFE filter and ZrCa-CED, respectively, (5) elution of interfering substances, and (6) fixation of the disks on acrylic plates and covering by cellophane tape.

PTFE filter, and As(V) by the lower ZrCa-CED. The disks were washed with 0.5 mL of a pH 3 HCl solution, and then separated. Each SPE disk was affixed to an acrylic plate (47 mm diameter and 10 mm thickness) with adhesive cellophane tape (15 mm width and 50 μ m thickness).

3.2.5 *Determination procedure*

SPE disks on acrylic plates were dried at 100°C for 15 min in an electric oven. The specimen was fitted to a sample holder (50 mm diameter), and then analyzed using a wavelength dispersive XRF spectrometer. The concentrations of As(III) and As(V) were calculated using the calibration curves previously constructed using a set of standard SPE disks.

3.3 Results and discussion

3.3.1 *Sample pH*

The pH dependence of adsorption rates of As(III) and As(V) collected on a PTFE filter and a ZrCa-CED was investigated. Twenty five milliliter of water samples containing 0.3 mmol APDC and 5 μ g of As(III) or As(V) were adjusted to pH 2–7 with HCl or NaOH solution. The adsorption rate of As on the SPE miniature disk was calculated from the difference between the As concentrations in the initial solution and the filtrate, which was measured by GFAAS. The pH dependencies of the adsorption rates for As(III) and As(V) are shown in Fig. 8. As(III) was adsorbed quantitatively at pH 2–3, but As(V) was not adsorbed by the PTFE filter, indicating that PTFE filters can be used to separate As(III) from As(V) at pH 2–3. The pH dependence of the adsorption rate of As(III) collected on a PTFE filter is the result of the As(III)-PDC complexation. A non-polar interaction mechanism is considered to be responsible for the adsorption of As(III)-PDC by a PTFE filter [53]. The ZrCa-CED adsorbed As(V) completely at pH 2–7. The adsorption is a complex-forming reaction between As(V) and the Zr of the ZrCa-CED. In addition, Ca in the ZrCa-CED inhibits the elution of As(V) [51]. Therefore, a sample solution of pH 2–3 was adopted for the separation of As(III) and As(V) in water.

3.3.2 *Sample flow rate*

The influence of the flow rate on the adsorption rates of the 5 μ g analytes was investigated. As shown in Fig. 9, All of As(III)-PDC was adsorbed at flow rates of 5–20

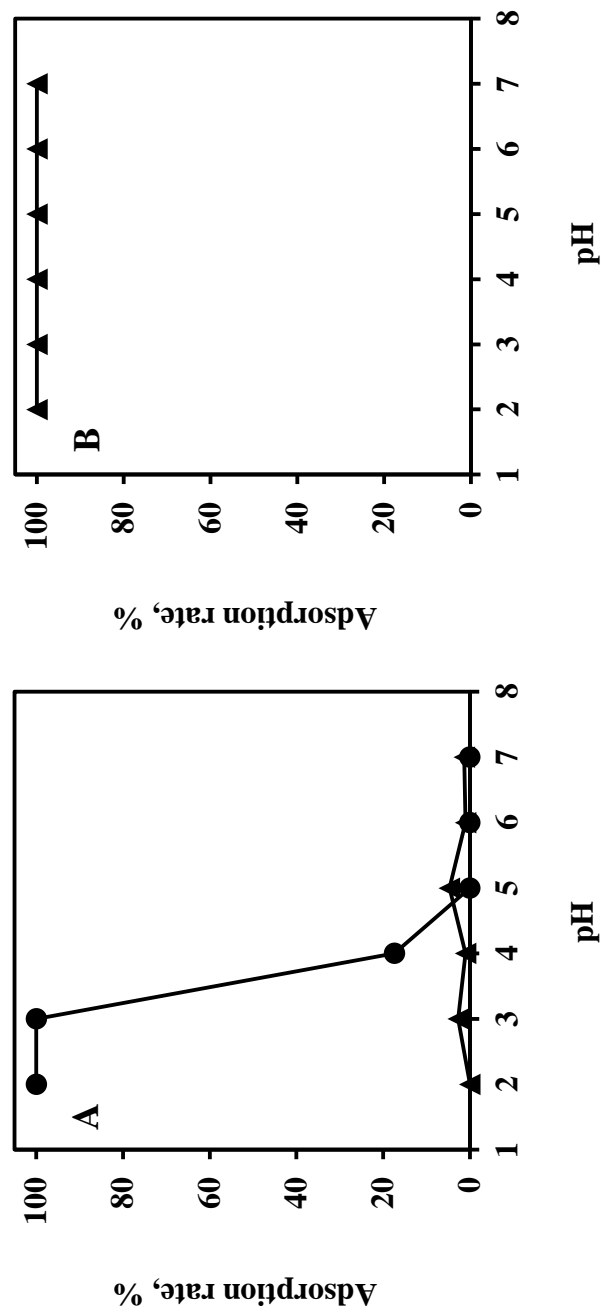


Fig. 8 Adsorption rates of As(III)-PDC (●) and As(V) (▲) at different pH values on (A) a PTFE filter and (B) a ZrCa-CED, respectively.

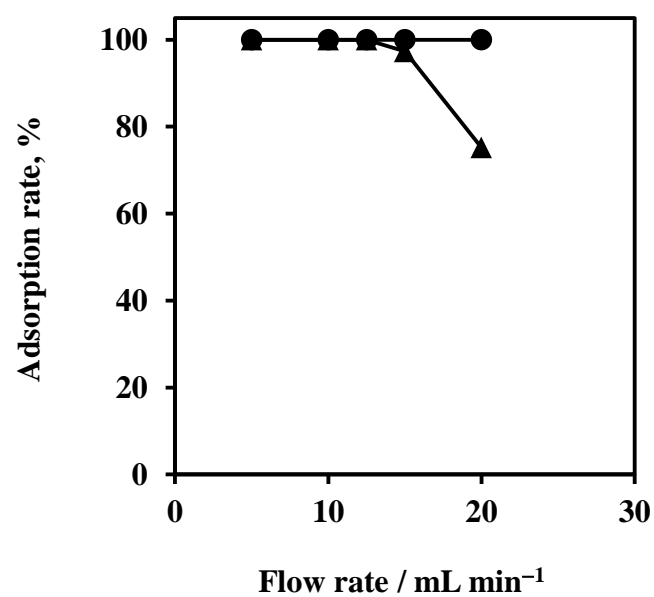


Fig. 9 Adsorption rates of As(III)-PDC (●) and As(V) (▲) at different solution flow rates on a PTFE filter and a ZrCa-CED, respectively.

mL min^{-1} , but the adsorption rate of As(V) was insufficient for a flow rate above 12.5 mL min^{-1} . Therefore, a sample flow rate of 12.5 mL min^{-1} or less is required to collect the analytes using the two SPE miniature disks.

3.3.3 Preservation

The preservation of the SPE miniature disks was investigated after the sample was kept for a month in ambient atmosphere. The fluorescent X-ray intensities of $2 \text{ }\mu\text{g}$ of As(III) collected on a PTFE filter and $2 \text{ }\mu\text{g}$ of As(V) collected on a ZrCa-CED were measured after storage for 0, 1, 2, 4, 8, 16, and 32 days. Although the X-ray intensities of each measurement were found to vary slightly, the relative standard deviations (0.67%–0.68%) of X-ray intensities were below the variation coefficient (1.4%) of X-ray counting. Consequently, the SPE miniature disks demonstrated sufficient preservative ability over a one month period. The proposed method is able to obtain accurate measurements of the concentration of As(III) and As(V) in water, even though considerable time may elapse between the preconcentration step and analysis by XRF spectrometry.

3.3.4 Calibration curve

Calibration curves of As(III) and As(V) for wavelength dispersive XRF were constructed from a set of standard SPE miniature disks. Figure 10 shows XRF spectra of 0, 0.5, 1, 2, 5 μg of As preconcentrated on PTFE filter and ZrCa-CED. Hf $\text{L}\gamma 1$ fluorescent line ($2\theta_{\text{LiF}(200)} = 34.04^\circ$) was found on the XRF spectra of blank ZrCa-CED, because zirconyl nitrate dihydrate for modifying the cation exchange disks contained Hf as an impurity. However, the amounts of Hf in every ZrCa-CEDs are same, so the As $\text{K}\alpha$ intensity of As(V) collected on a ZrCa-CED can be measured without correction. The calibration curves of As(III) and As(V) showed good linearity in the range of 0.5–5 μg . Linear equations for the calibration curves were determined by fitting to be $I = 0.118M - 0.0175$ ($r = 0.9997$) for As(III), and $I = 0.117M + 0.0468$ ($r = 0.9998$) for As(V), where I is the fluorescent X-ray intensity (kcps), M is the absolute amount (μg), and r is the correlation coefficient of the liner fit. The detection limits, defined as three times the standard deviation, as evaluated by its relationship to the slope of the calibration curve, were $0.04 \text{ }\mu\text{g}$ for As(III) and $0.03 \text{ }\mu\text{g}$ for As(V). Therefore, for a 50 mL water sample, the detection limits were $0.8 \text{ }\mu\text{g L}^{-1}$ for As(III) and $0.6 \text{ }\mu\text{g L}^{-1}$ for As(V). These values are lower than the maximum value of As ($10 \text{ }\mu\text{g L}^{-1}$) established by the WHO for drinking water. The detection limit of proposed method was found to be comparable with other

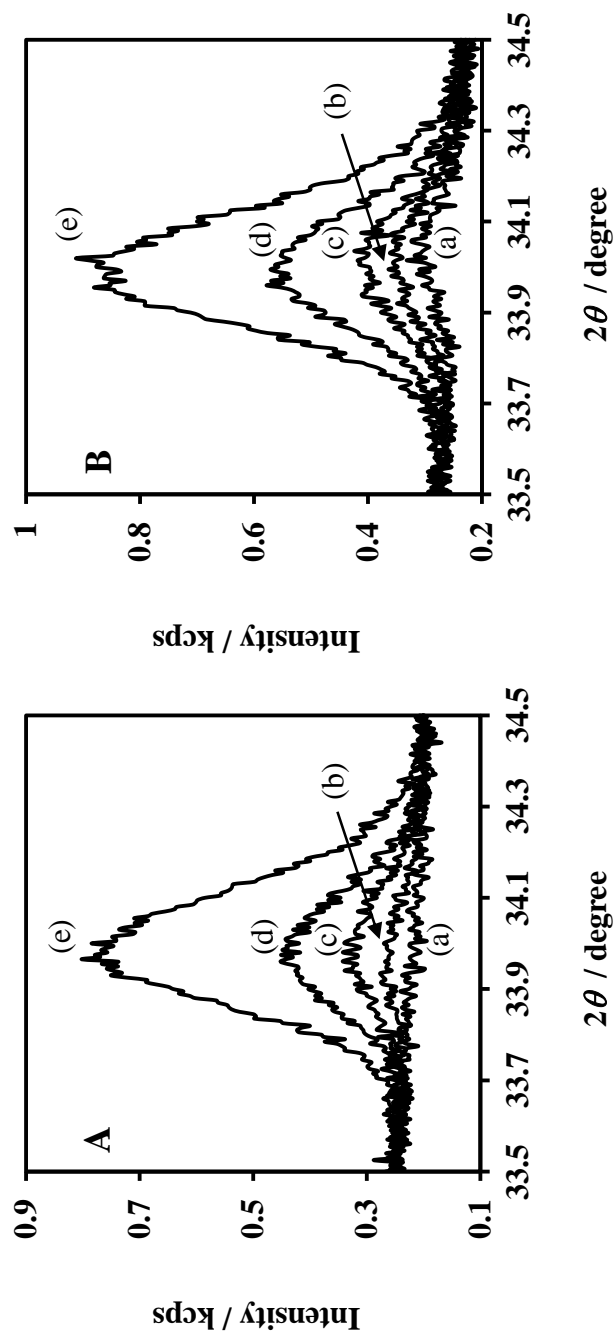


Fig. 10 XRF spectra of As K α of (A) As(III)-PDC collected on a PTFE filter, and (B) As(V) collected on a ZrCa-CED. (a): blank, (b): 0.5 μg , (c): 1 μg , (d): 2 μg , and (e): 5 μg of As.

values using SPE followed by AAS methods: SPE-flow injection HGAAS, $0.5 \mu\text{g L}^{-1}$ [13]; on-site SPE/HGAAS, $0.3 \mu\text{g L}^{-1}$ [38]; SPE/GFAAS, $0.1 \mu\text{g L}^{-1}$ [34].

3.3.5 Removal of lead from sample water

Mutual interference between the As $K\alpha$ and Pb $L\alpha$ fluorescent lines occurs because of their close proximity to each other (*i.e.*, $2\theta_{\text{LiF}(200)} = 33.98^\circ$ for As $K\alpha$ and $2\theta_{\text{LiF}(200)} = 33.92^\circ$ for Pb $L\alpha$). As such, if As(III) and As(V) coexist with Pb^{2+} in sample water, this overlap may cause serious analytical error because both APDC [53] and the cation exchange disk used in the present study react with Pb^{2+} . This problem could be solved by measuring the As $K\beta$ line intensity for determining As. However, the intensity of As $K\beta$ line is minuscule relative to that of the As $K\alpha$ line, which would prohibit the determination of $\mu\text{g L}^{-1}$ levels of As in water. It is also possible to evaluate the Pb $L\alpha$ line intensity relative to the As $K\alpha$ line intensity using Pb $L\beta$ line intensity, and to apply this as a correction of the As $K\alpha$ line intensity [21, 54]. However, water samples typically contain selenite as well, which reacts with both APDC [34, 55] and Zr [56], and the Se $K\beta$ line overlaps with the Pb $L\beta$ line. Consequently, the intensity of the Pb $L\beta$ line must be similarly corrected with respect to the intensity of the Se $K\alpha$ line. Therefore, XRF measurements of three angles and the multilevel correction illustrated in Fig. 11 would be necessary to obtain a quantitative value of As by this method. For a much easier determination of As using XRF spectrometry, it was decided to first remove Pb^{2+} from the water samples using a chelating disk. As shown in Fig. 12, the As $K\alpha$ intensity (b) of the SPE disk spiked with equivalent amount of As and Pb without pretreatment using a chelating disk was about 1.4 times that of the normal As $K\alpha$ line intensity (a) with no Pb. However, when Pb^{2+} in the sample water was removed using a chelating disk before the collection of As, the As $K\alpha$ line intensity (c) of the SPE disk was equivalent to that of the normal As $K\alpha$ line intensity (a). In most cases, As(III) and As(V) were not adsorbed by the chelating disk because these As species are anions and/or neutral forms in the sample solution. However, As(III) and As(V) were found to be partially adsorbed on the chelating disk when Al^{3+} and Fe^{3+} coexisted in the sample water, indicating that the As species reacts with Al [57] and Fe [58] collected by the chelating disk. This problem was resolved by the elution of As using 0.5 mL of a pH 13 NaOH solution. By so doing, As(III) and As(V) were completely eluted and then recovered by the mixture of the eluate and filtrate.

The pH dependences of the adsorption rates for $5 \mu\text{g}$ of As(III), As(V), and Pb^{2+} collected on a chelating disk concluding the elution using the NaOH solution was investigated. As shown in Fig. 13, Pb^{2+} was not eluted at all using the 0.5 mL of a pH 13

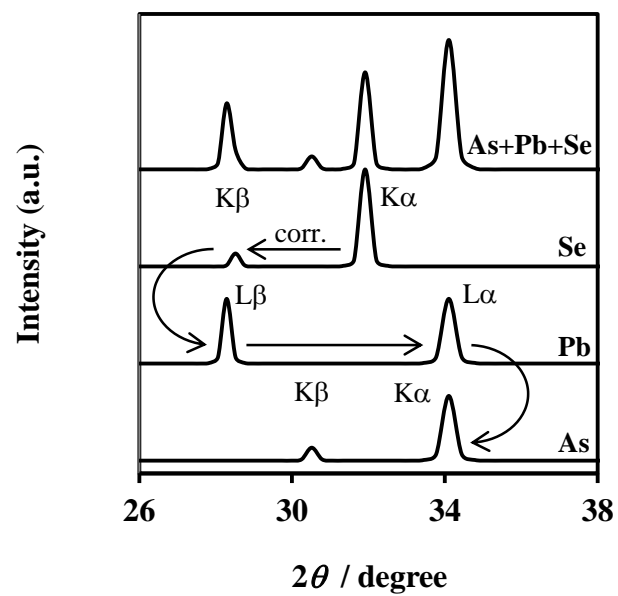


Fig. 11 Mutual interferences of As, Pb and Se XRF spectra, and the multilevel correction required to obtain a quantitative value for the As $K\alpha$ line intensity.

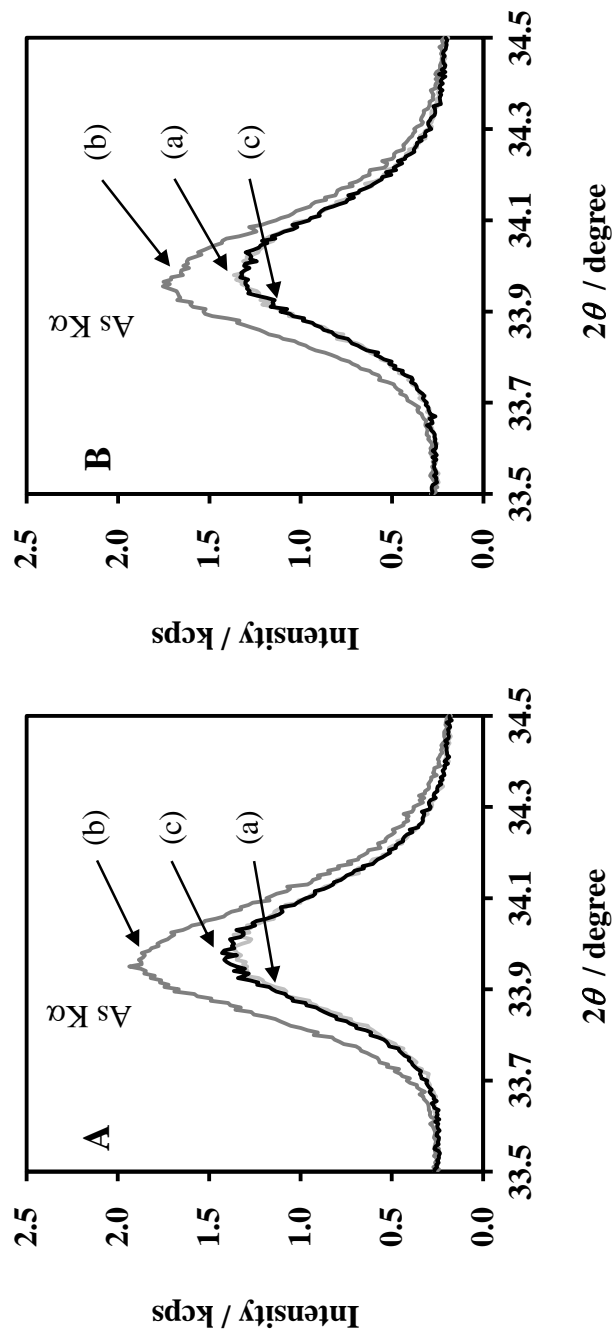


Fig. 12 XRF spectra of (A) As(III)-PDC collected on a PTFE filter, and (B) As(V) collected on a ZrCa-CED under the following conditions.

- (a): 10 μg of As spiked without pretreatment using a chelating disk.
- (b): 10 μg of As and 10 μg of Pb^{2+} spiked without pretreatment using a chelating disk.
- (c): 10 μg of As and 10 μg of Pb^{2+} spiked with pretreatment using a chelating disk.

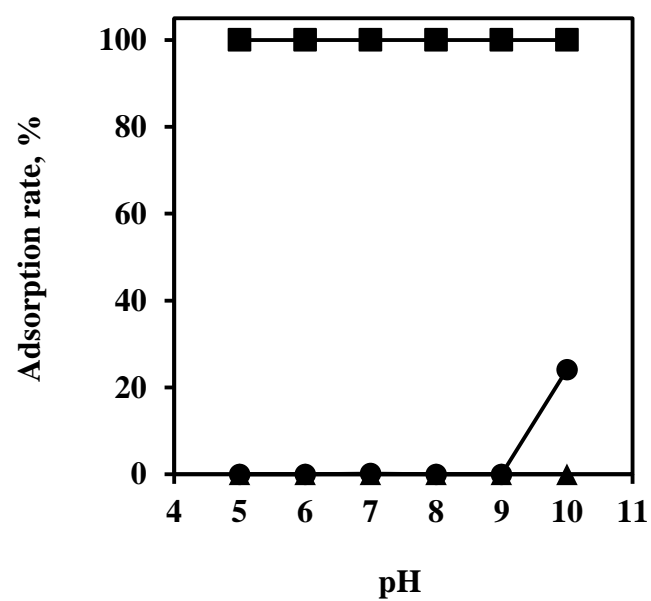


Fig. 13 Adsorption rates of As(III) (●), As(V) (▲), and Pb²⁺ (■) at different pH values on a chelating disk.

NaOH solution, and was removed completely for a sample flow rate of 20 mL min⁻¹ by the chelating disk without the loss of As at pH 5–9. This pH range nearly covers the entire pH range of drinking water. Moreover, the pore size of the SPE disk is very small, so the chelating disk was useful for the simultaneous removal of Pb²⁺ and suspended matter in the water samples.

3.3.6 Influence of coexisting ions

A spike test was conducted for 0.5 µg of As(III) and As(V) in 50 mL of artificial freshwater containing 5 mg L⁻¹ of Na⁺, 3 mg L⁻¹ of K⁺, 5 mg L⁻¹ of Mg²⁺, 50 mg L⁻¹ of Ca²⁺, 10 mg L⁻¹ of Cl⁻, and 20 mg L⁻¹ of SO₄²⁻. The recoveries of As(III) and As(V) were 97% and 98%, respectively, in this solution. As such, the concentrations of typical major ions found in freshwater did not interfere with the recoveries of the analytes. The effects of minor ions found in fresh water on the recoveries of As(III) and As(V) were also tested. When 0.5 µg of As(III) and As(V) were added to 50 mL of test water coexisting with 100 µg L⁻¹ of Al³⁺, 10 µg L⁻¹ of V⁵⁺ (H₂VO₄⁻), 10 µg L⁻¹ of Cr³⁺ (H₂CrO₂⁺), 10 µg L⁻¹ of Mn²⁺, 100 µg L⁻¹ of Fe³⁺, 10 µg L⁻¹ of Ni²⁺, 10 µg L⁻¹ of Cu²⁺, 100 µg L⁻¹ of Zn²⁺, 300 µg L⁻¹ of Sr²⁺, and 10 µg L⁻¹ of Pb²⁺, the recoveries of As(III) and As(V) were 108% and 107%, respectively. Cu²⁺ and Pb²⁺ retard the complexation of As(III)-PDC [59], and Fe³⁺ affects the adsorption of As(V) on Zr loaded resin [39], as reported previously. However, minimal interferences were observed in the present study because the interfering cations in the sample were removed by the chelating disk. Next, the effect of organic arsenics (10 µg L⁻¹ diphenylarsenic acid and phenylarsonic acid) on the recoveries of arsenic compounds was investigated. As(III) was recovered quantitatively (94%–108%), but the recovery of As(V) were 120%–127%. Organic arsenics and Pb in the water sample will be removed simultaneously by a chelating disk based on activated carbon.

3.3.7 Applications

To evaluate the quantitative performance of the proposed method, spike tests were performed for As(III) and As(V) in natural mineral water sampled at Kanagawa, Japan. The results of the spike tests are listed in Table 4. Good recoveries of 98%–104% were obtained, indicating that the proposed method was useful for determining µg L⁻¹ levels of As in drinking water.

The proposed screening method was applied to determine As(III) and As(V) in spring water and well water samples collected at the area of 613 km² in a northern Chiba, Japan. Fourteen SPE samples were collected at 19 sites (the water samples were not collected at 5

Table 4 Spike tests for As(III) and As(V) added to natural mineral water

Sample	Added / $\mu\text{g L}^{-1}$		Found / $\mu\text{g L}^{-1}$		Recovery, %	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Natural mineral water	0	0	N.D.	N.D.	–	–
	10.0	0	10.0 (5.3)	N.D.	100	–
	0	10.0	N.D.	9.8 (3.8)	–	98
	10.0	10.0	10.4 (3.9)	10.4 (6.3)	104	104

N.D.: Not detected.

(): Relative standard deviation, % ($n = 3$).

sites due to the drought), and immediately treated using the proposed on-site preconcentration method. The time required for travel, sampling, and pretreatment was 15 h, and the analyses required 2.5 h. The analytical results are presented in Table 5. The highest concentration of As(III) found was $1.5 \mu\text{g L}^{-1}$ for the sample denoted as well water 1, and that of As(V) was $7.5 \mu\text{g L}^{-1}$ for well water 3. The total As concentrations (As(III) + As(V)) of all sites fell below the drinking water standard set by the WHO ($10 \mu\text{g L}^{-1}$). The dominant species was As(III) for 6 of the sites considered, whereas As(V) was dominant for 1 site. The concentrations of arsenic species in ground water are controlled by many factors including the source of the arsenic and water quality. In regards to pH, temperature and/or dissolved oxygen, no relationships were observed at any of the sites considered.

Table 5 Analytical results of As(III) and As(V) in drinking water sampled at northern Chiba, Japan

Sample	Concentration / $\mu\text{g L}^{-1}$		pH	Temperature / $^{\circ}\text{C}$	Dissolved oxygen / mg L^{-1}
	As(III)	As(V)			
Spring water 1	1.2	N.D.	6.22	18.0	4.35
Spring water 2	N.D.	N.D.	6.63	17.4	5.05
Spring water 3	N.D.	N.D.	7.26	18.9	5.96
Spring water 4	N.D.	N.D.	7.57	19.6	4.35
Well water 1	1.5	N.D.	8.53	20.4	0.06
Spring water 5	N.D.	N.D.	9.23	16.5	0.01
Well water 2	0.9	N.D.	8.90	15.8	0.01
Spring water 6	N.D.	N.D.	8.66	15.7	0.02
Spring water 7	1.1	N.D.	8.09	15.9	5.47
Spring water 8	N.D.	N.D.	8.32	17.1	4.04
Spring water 9	0.9	N.D.	7.82	15.5	5.01
Spring water 10	N.D.	N.D.	7.52	15.1	4.63
Well water 3	1.0	7.5	8.49	14.3	1.39
Spring water 11	1.4	N.D.	8.02	15.8	4.13

N.D.: Not detected.

Chepter 4 On-site determination of total arsenic in water by disk solid-phase extraction/mobile X-ray fluorescence spectrometry

4.1 On-site analytical methods of arsenic in water

Sensitive analytical methods using various instrumental techniques, such as ICP-MS, ICP-AES, GFAAS, and HGAAS have been used for the determination of As in water [5]. However, the analysis time after sampling is long because these methods required transport of water samples to a laboratory.

SV [46, 60] and colorimetry [48, 61–66] have been developed for the on-site determination of inorganic As in water. However, SV requires a power supply, an As standard solution for calibration, and a reduction with heating in the field. The Gutzeit method is a popular colorimetric method for As detection [61, 62], and field test kits using this method are available [63]. However, field workers must be careful because the Gutzeit method generates poisonous arsine gas [64]. Colorimetric methods without the generation of arsine have also been developed [47, 48, 65, 66]. These use coloring reagents that react with As(III) or As(V) in water and an oxidation and/or reduction for the determination of total inorganic As.

Mobile XRF spectrometer, which is also called portable field XRF spectrometer or handheld XRF spectrometer, is rechargeable type portable element analyzer, and is commonly used for the on-site screening of solid samples. If mobile XRF spectrometry could evaluate the concentrations of chemical substances in environmental water, the investigation of water quality could be conducted simultaneously with a survey of the surrounding environment such as soil [67, 68], minerals [69, 70], and waste [71] in the field. This would be helpful in the rapid specification and removal of pollutant sources. To determine $\mu\text{g L}^{-1}$ levels of an element in water, XRF spectrometry is usually used in combination with a preconcentration method, *e.g.*, evaporation, coprecipitation, and extraction [72]. Membrane disk type SPE can be easy combined with XRF spectrometry, and several methods using this technique have been developed for the screening of trace elements in water [19, 20, 73]. Although an on-site analytical method combining disk SPE with mobile XRF spectrometry has been applied to the determination of cationic heavy metals in water [52], As determination by this method has not been reported.

Herein, a method for the on-site determination of As in drinking water using membrane disk SPE followed by mobile XRF spectrometry is described. This method involved the pre-concentration of As on a Ti and Zr-loaded carbon disk (TiZr-CD). The discussion covers: the preparation of the TiZr-CD; the optimum sample pH, flow rate, and desiccation

time; the calibration curve; the effect of coexisting ions; and the determination of organic As. The proposed method was successfully used to determine the total As in well water.

4.2 Experimental

4.2.1 Apparatus

A Niton XL3t GOLDD+ analyzer (Thermo Fisher Scientific, Waltham, USA) equipped with a Ag X-ray tube (voltage: 6–50 kV and current: 0–200 μ A) and a silicon drift detector was employed for the mobile XRF spectrometry. The measurements of As $K\alpha$ intensity were performed using a plastic analysis mode (8 mm collimation) under atmospheric conditions for 120 s.

A ZEE nit 600s graphite furnace atomic absorption spectrometer (Analytik jena AG) was used for the determination of As and Pb in water. Measurement conditions are listed in Table 6.

A Demi-Ace Model DX-15 demineralizer (Kurita Water Industries) was used to prepare the deionized water. An F-52 pH meter (Horiba) was used to control the pH of the test solution. An LB-351 cordless hair iron (Hi Make, Aichi, Japan) was used for drying the SPE disks.

4.2.2 Reagents and samples

A 1000 mg L^{-1} As(III) stock solution (pH 5) was prepared by dissolving arsenic(III) oxide (99%; Junsei Chemical) in a 0.1 mol L^{-1} NaOH solution, and then adding 1 mol L^{-1} HCl and deionized water. A 1000 mg L^{-1} As(V) stock solution was prepared by dissolving disodium hydrogen arsenate heptahydrate (99%; Junsei Chemical) in deionized water. All organic arsenic compounds were obtained from Wako Pure Chemical Industries unless otherwise indicated. MAA (95%) and DPAA (99.6%) stock solutions (10 mg L^{-1}) were prepared in deionized water. DMAA (sodium salt, 97%), PAA (96%), *p*-AA (98%; Kanto Chemical), and Rox (99%) stock solutions (100 mg L^{-1}) were prepared in deionized water. A 1000 mg L^{-1} Pb^{2+} stock solution was prepared by dissolving lead nitrate (99.3%; Kanto Chemical) in deionized water. Titanium isopropoxide (first grade; Tokyo Chemical Industry, Tokyo, Japan) and zirconium propoxide (70% in 1-propanol; Tokyo Chemical Industry) were used to modify the carbon disks. All of the other reagents were of extra pure grade.

Table 6 Instrumental conditions for graphite furnace atomic absorption spectrometer for As and Pb determination

Apparatus	Analytik jena AG ZEE nit 600s	
Element	As	Pb
Analytical line / nm	193.7	283.3
Lamp current / mA	8	4
Slit width / nm	1.2	0.8
Drying / °C	90–110 (62)	90–110 (62)
Pyrolysis / °C	1000 (24)	900 (13)
Atomization / °C	2500 (4)	2400 (4)
Cleaning / °C	2600 (3)	2600 (3)
Injection volume / µL	20	10
Matrix modifier	Pd	–
Absorbance	Peak area	
Background correction	Zeeman	

(): Heating time / s

Carbon disks (EmporeTM Activated Carbon; 47 mm diameter, and 0.5 mm thickness; 3M) were used throughout this study. They were cut to a 13 mm diameter before use. The sample water was passed through the miniature SPE disk by pressurization using a plastic syringe with a filter holder.

Well water samples were obtained from Kujukuri, Chiba, Japan. They were filtered through a GMF-150 glass fiber filter (1.0 μm pore size, 47 mm diameter, 0.73 mm thickness; Whatman) and analyzed immediately using the proposed method.

4.2.3 *Preparation of titanium and zirconium loaded carbon disks*

Ten carbon disks (*ca.* 0.5 g) were stirred in 15 mL of ethanol containing 1 mL of titanium isopropoxide and 0.5 mL of 70% zirconium propoxide for 5 min. The SPE disks were then soaked in deionized water and used within 24 h.

4.2.4 *Preconcentration and determination procedures*

A 50 mL water sample was adjusted to pH 3 using 0.1 mol L⁻¹ HCl, and then passed through a TiZr-CD at a flow rate of ≤ 20 mL min⁻¹ to preconcentrate the As. The SPE disk was adhered to an acrylic plate (47 mm diameter and 10 mm thickness) with adhesive cellophane tape (15 mm width and 50 μm thickness), and then analyzed using a mobile XRF spectrometer. The As concentrations were calculated using a calibration curve that was previously constructed using a set of standard As(III)-loaded SPE disks.

4.3 Results and discussion

4.3.1 *Preparation of solid-phase extraction disks*

Adsorption materials that are loaded with Ti [74, 75] or Zr [39, 51, 56, 73, 75,] were able to collect As in water because of complex formation between As and the modifier metals. Therefore, the ability of a Ti and/or Zr-loaded carbon disks to quantitatively adsorb As(III) and As(V) was investigated. The SPE disks were prepared as follows: carbon disks were stirred in 15 mL of ethanol containing 0–1 mL of titanium isopropoxide and 0–1 mL of 70% zirconium propoxide for 5 min, and then were soaked in deionized water. Water samples (50 mL) containing 5 μg of As(III) or As(V) were passed through the SPE disks at a flow rate of 5 mL min⁻¹. The adsorption rate of As on the SPE disk was calculated using the difference between the As concentrations in the initial solution and the filtrate, which was measured by GFAAS. The adsorption rates of As(III) and As(V) on the SPE disks are

given in Table 7. The disk loaded with 1 mL of titanium isopropoxide quantitatively adsorbed As(III), but only adsorbed about 70% of the As(V). In contrast, the disk loaded with 0.5 mL of 70% zirconium propoxide quantitatively adsorbed As(V), but only adsorbed half of the As(III). When 1 mL of 70% zirconium propoxide was used for the preparation of a Zr-loaded carbon disk, the adsorption rate of the As(III) did not increase. However, As(III) and As(V) were completely adsorbed by the TiZr-CD, which was produced using 1 mL of titanium isopropoxide and 0.5 mL of 70% zirconium propoxide. Therefore, in subsequent extractions, As was extracted with this TiZr-CD.

4.3.2 Sample pH

The pH dependence of the adsorption rates of 5 μg of As(III) and As(V) collected onto a TiZr-CD was investigated. The pH of the sample solutions was adjusted to pH 2–10 with HCl or NaOH solutions. The pH dependence of the adsorption rates of As(III) and As(V) are shown in Fig. 14-A. The TiZr-CD adsorbed As(III) and As(V) quantitatively under pH 3–9 and pH 2–8, respectively.

Mutual interference between the As $K\alpha$ and Pb $L\alpha$ X-ray fluoresce lines occurs because of their close proximity (*i.e.*, 10.54 keV for As $K\alpha$ and 10.55 keV for Pb $L\alpha$). It is possible to evaluate the Pb $L\alpha$ intensity relative to the As $K\alpha$ intensity using the Pb $L\beta$ intensity, and thereby correct As $K\alpha$ intensity. However, if the ratio of the As $K\alpha$ and Pb $L\alpha$ intensities is very small, error may occur. To facilitate an accurate determination of As using mobile XRF spectrometry, the pH range at which 5 μg of Pb^{2+} was not adsorbed by the TiZr-CD was investigated. As shown in Fig. 14-B, Pb^{2+} was not adsorbed by the TiZr-CD at pH 2–3, but was adsorbed quantitatively at pH 5–10. Therefore, sample solutions at pH 3, where Pb^{2+} was not adsorbed by the TiZr-CD, were adopted for the preconcentration of As in water.

4.3.3 Sample flow rate

The influence of the flow rate on the adsorption rates of the 5 μg analytes samples was investigated. As shown in Fig. 15, all of the As(III) was adsorbed at flow rates from 5–25 mL min^{-1} , but the adsorption rate of As(V) was insufficient at a flow rate $>20 \text{ mL min}^{-1}$. Therefore, a sample flow rate of $\leq 20 \text{ mL min}^{-1}$ was required for the quantitative collection of As(III) and As(V) using the SPE disks. In subsequent study, sample water was passed through the TiZr-CD at a flow rate of 10 mL min^{-1} .

Table 7 Adsorption rate of As(III) and As(V) with respect to modifier material volumes in 15 mL of ethanol for the preparation of SPE disks

Titanium isopropoxide	Modifier material volume / mL		Adsorption rate, %	
	70% zirconium propoxide	As(III)	As(V)	
0.5	0	62	70	
1.0	0	100	74	
0	0.5	51	100	
0	1.0	66	100	
1.0	0.5	100	100	

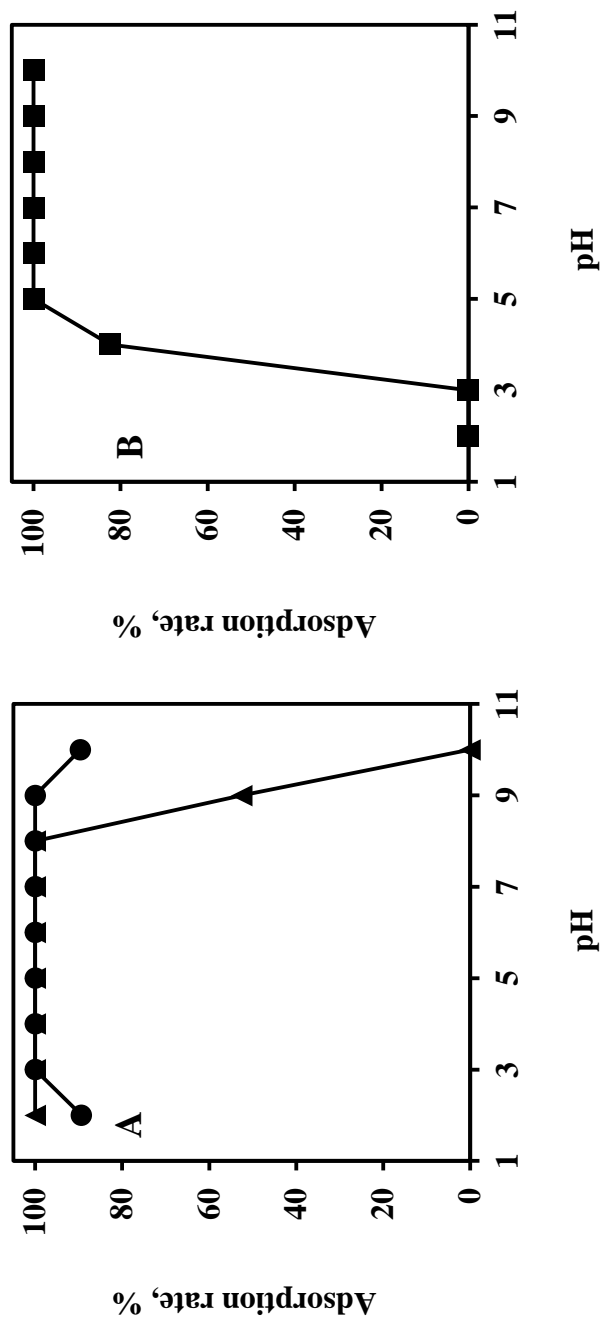


Fig. 14 Adsorption rates of As(III) (●), As(V) (▲) and Pb²⁺ (■) at different pH values on a TiZr-CD.

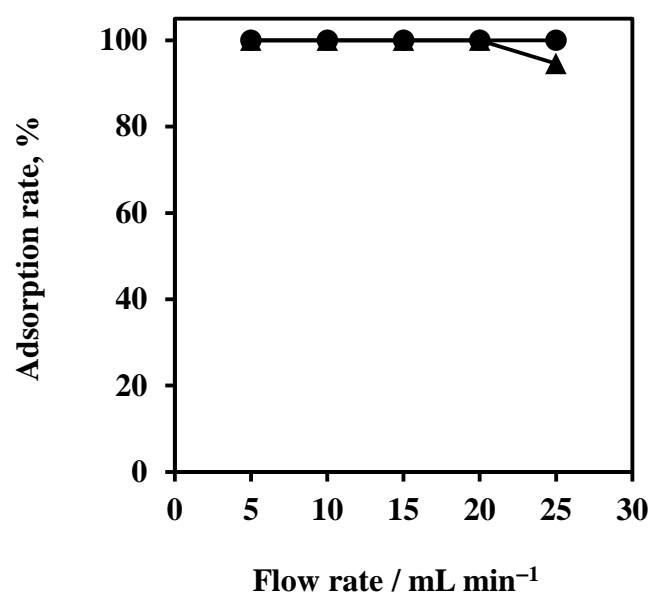


Fig. 15 Adsorption rates of As(III) (●) and As(V) (▲) at different solution flow rates on a TiZr-CD.

4.3.4 Desiccation of solid-phase extraction disk

The X-ray fluorescence intensity of an element can vary with the amount of moisture in the sample [76], therefore, samples are generally dried prior to XRF measurement. In particular, the desiccation time is a significant factor in speed and accuracy of field measurement. Therefore, the influence of the desiccation time on the X-ray fluorescence intensity of As was investigated. Variations in the As $K\alpha$ intensity and the weight of TiZr-CD containing 2 μg of As(V) vs. desiccation times at 100°C are shown in Fig. 16. The weight of the TiZr-CD decreased markedly with an increase in desiccation time, and the water content of SPE disks was thoroughly removed after >90 s. However, As $K\alpha$ intensity did not vary significantly with desiccation time; the relative standard deviation of As $K\alpha$ intensity for 0–120 s of desiccation was only 3.5%. Therefore, water content did not affect As $K\alpha$ intensity, and desiccation of the SPE disk was unnecessary.

4.3.5 Calibration curve

Calibration curves for As(III) and As(V) for the mobile XRF spectrometry were constructed using a set of standard SPE disks. Figure 17 shows the XRF spectra of 0, 0.5, 1, 2, and 5 μg of As(III) and As(V) preconcentrated onto TiZr-CD. The calibration curves of As(III) and As(V) had good linearity over the range of 0.5–5 μg . The linear equations for the calibration curves were determined by linear regression to be $I = 0.249M + 0.418$ ($r = 0.999$) for As(III), and $I = 0.249M + 0.416$ ($r = 0.999$) for As(V), where I is the X-ray fluorescence intensity ($\text{cps } \mu\text{A}^{-1}$), M is the absolute amount of As (μg), and r is the correlation coefficient of the linear fit. The detection limits, which are defined as three times the standard deviation, as evaluated by its relationship to the slope of the calibration curve, were 0.10 μg for both As(III) and As(V). Therefore, for a 50 mL water sample, the As detection limit was 2.0 $\mu\text{g L}^{-1}$. This value is lower than the maximum value of As (10 $\mu\text{g L}^{-1}$) recommended by the WHO for drinking water, and the detection limit of the proposed method was found to be comparable with that obtained using ICP-AES (3.0 $\mu\text{g L}^{-1}$) [77].

4.3.6 Influence of coexisting ions

A spike test was conducted for 2 μg of As(III) and As(V) in 50 mL of artificial water containing 5 mg L^{-1} of Na^+ , 3 mg L^{-1} of K^+ , 5 mg L^{-1} of Mg^{2+} , 50 mg L^{-1} of Ca^{2+} , 10 mg L^{-1} of Cl^- , and 20 mg L^{-1} of SO_4^{2-} , which imitating freshwater in Japan [43]. Recoveries of As(III) and As(V) in this solution were 107% and 105%, respectively. The effects of minor ions found in freshwater on the recoveries of As(III) and As(V) were also evaluated.

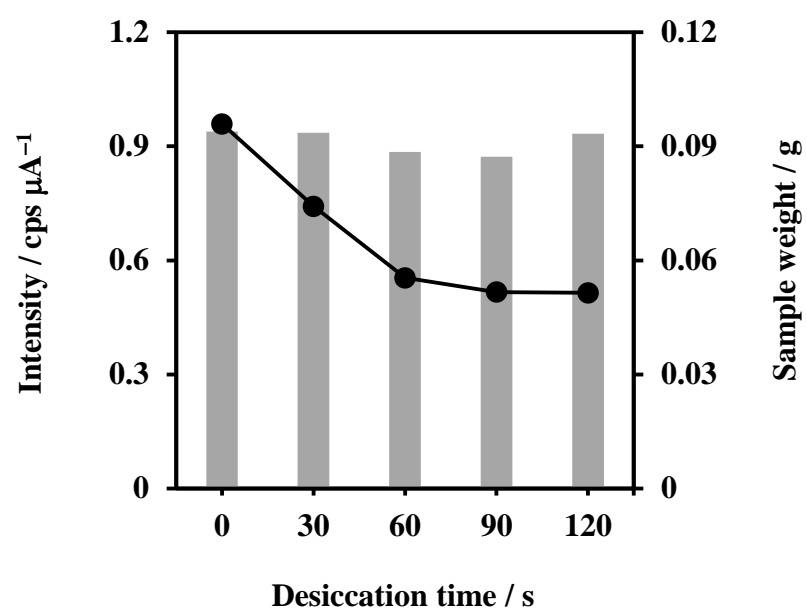


Fig. 16 Variations in the As $K\alpha$ intensity of 2 μg As(V) (bar chart) and the sample weight (●) with desiccation times at 100°C.

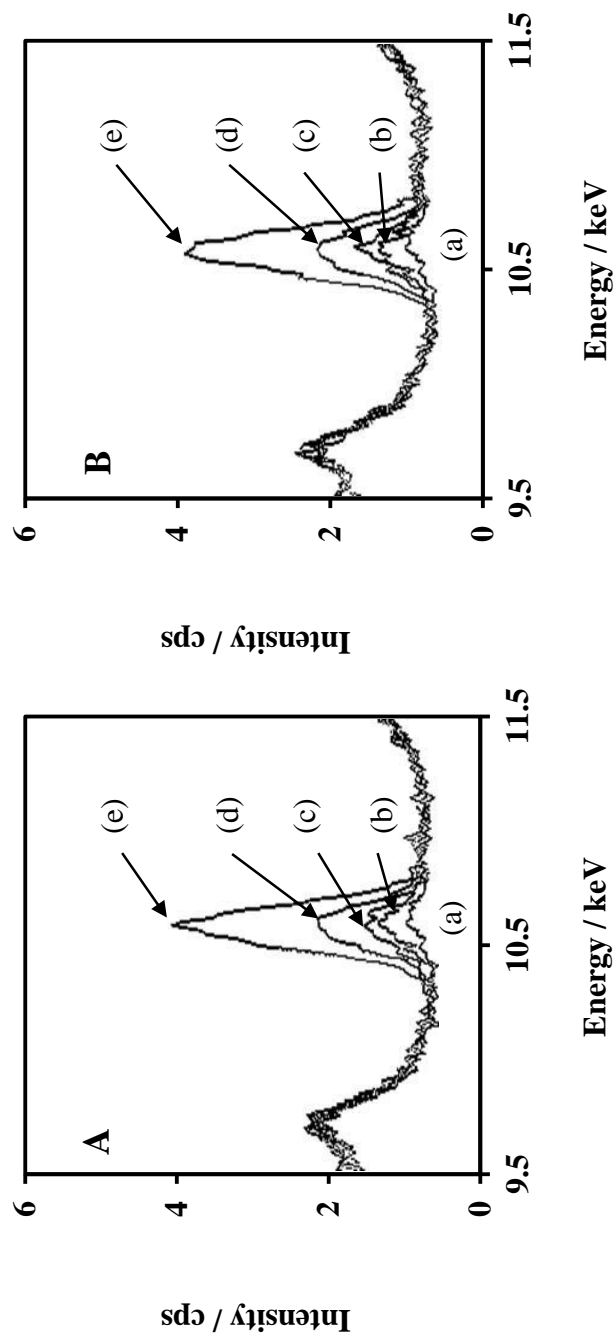


Fig. 17 XRF spectra of K α of (A) As(III) and (B) As(V) collected on a TiZr-CD. (a): blank, (b): 0.5 μ g, (c): 1 μ g, (d): 2 μ g, and (e): 5 μ g of As.

When 2 μg of As(III) and As(V) were added to 50 mL of test water containing 100 $\mu\text{g L}^{-1}$ of Al^{3+} , 10 $\mu\text{g L}^{-1}$ of V^{5+} (H_2VO_4^-), 10 $\mu\text{g L}^{-1}$ of Cr^{3+} (H_2CrO_2^+), 10 $\mu\text{g L}^{-1}$ of Mn^{2+} , 100 $\mu\text{g L}^{-1}$ of Fe^{3+} , 10 $\mu\text{g L}^{-1}$ of Ni^{2+} , 10 $\mu\text{g L}^{-1}$ of Cu^{2+} , 100 $\mu\text{g L}^{-1}$ of Zn^{2+} , 300 $\mu\text{g L}^{-1}$ of Sr^{2+} , and 10 $\mu\text{g L}^{-1}$ of Pb^{2+} , the recoveries of As(III) and As(V) were 107% and 108%, respectively. As such, the concentrations of the major and minor ions typically found in freshwater did not interfere with inorganic As recovery.

4.3.7 Determination of organic arsenic

Ground water contaminated with organic As has been found in recent years [2, 3]. Therefore, it is desirable that total As, which is comprised of both inorganic and organic As, in water can be determined. To evaluate the quantitative performance of the proposed method for the determination of organic As, spike tests were performed using MAA, DMAA, PAA, DPAA, *p*-AA, and Rox in water. The result of the spike tests are listed in Table 8. Good recoveries were obtained at 88%–106%, which indicated that the proposed method was also useful for determining organic As, such as methyl, phenyl and aromatic As in water. The adsorptions of organic As occurred because of the hydrophobic interactions between the organic groups of organic As and the activated carbon, besides the complex forming reaction between arsenate group of organic As and the modifier metals.

4.3.8 Applications

The proposed method was applied to the determination of As in drinking water. Table 9 presents the analytical results for As in seven well water samples from Kujukuri, Chiba, Japan. The values obtained using the GFAAS method for liquid samples are given for comparison. The concentrations of As obtained with the proposed method concurred with those obtained with the GFAAS method, and the relative errors were $\leq 7.9\%$. To evaluate the repeatability of the proposed method, four SPE samples were prepared using well water 7 (37.6 $\mu\text{g L}^{-1}$ of As obtained with GFAAS method) and then analyzed by mobile XRF spectrometry. The relative standard deviation was 2.4%, so the reproducibility of the proposed method is sufficient.

Table 8 Recovery of organic As from spiked samples

As species	Added ^a / $\mu\text{g L}^{-1}$	Found ^a / $\mu\text{g L}^{-1}$	Recovery, %
Methylarsonic acid	40.0	42.3	106
Dimethylarsinic acid	40.0	35.0	88
Phenylarsonic acid	40.0	42.3	106
Diphenylarsinic acid	40.0	37.5	94
<i>p</i> - Arsanilic acid	40.0	39.5	99
Roxarsone	40.0	38.8	97

^a As concentration.

Table 9 Analytical results of As in well water sampled at Kujukuri, Japan

Sample	Concentration / $\mu\text{g L}^{-1}$		Relative error, %
	Proposed method	GFAAS	
Well water 1	<2.0 ^a	<0.7 ^a	–
Well water 2	7.3	7.4 (7.8)	1.3
Well water 3	9.6	8.9 (3.0)	7.9
Well water 4	12.1	11.4 (1.3)	6.1
Well water 5	15.1	14.5 (7.3)	4.1
Well water 6	20.3	20.6 (5.7)	1.5
Well water 7	37.7 (2.4)	37.6 (2.6)	0.3

^a Not detected.

(): Relative standard deviation, % ($n = 4$).

Chapter 5 Conclusion

A simple method combining disk SPE with GFAAS is proposed for the determination of DPAA, PAA, and inorganic As in drinking water. Three kinds of SPE disks, an Empore SDB-XD disk as the upper layer, an activated carbon disk as the middle layer, and a Cation-SR disk loaded with Zr and Ca as the lower layer, were stacked together, and used to separate and concentrate DPAA, PAA, and iAs. DPAA, PAA, and iAs could be collected simultaneously and separately (on each disk) with one pass of the water sample, and the analytes could be determined using a single calibration curve by using a matrix modifier containing Pd and nitric acid for the GFAAS analysis. Spiked tests, with $10\ \mu\text{g L}^{-1}$ of DPAA, PAA, and iAs in tap water and natural mineral water, showed that quantitative recoveries were achieved.

A rapid and simple method combining on-site disk SPE with wavelength dispersive XRF spectrometry was proposed for determining inorganic As in drinking water. A hydrophilic PTFE filter, APDC, and ZrCa-CED were used for separating As(III) and As(V). As(III) and As(V) could be determined directly without an elution step. To avoid the overlapping Pb $L\alpha$ and As $K\alpha$ fluorescence line in wavelength dispersive XRF spectrometry, Pb was removed using a chelating disk before the separation of As(III) and As(V). Spike tests comprised of $10\ \mu\text{g L}^{-1}$ of As(III) and As(V) in natural mineral water demonstrated that quantitative recoveries were achieved. The proposed method was successfully applied to screening for the speciation and evaluation of the concentration of As in actual drinking water samples.

A rapid and simple method combining disk SPE with mobile XRF spectrometry was proposed for on-site determination of As in drinking water. The on-site analytical procedure consisted of only four processes: pH adjustment, preconcentration, immobilization of the SPE disk, and mobile XRF spectrometry. A TiZr-CD was used for collecting inorganic and organic As without requiring oxidation, reduction, or acid decomposition. The detection limit of As ($2.0\ \mu\text{g L}^{-1}$) was lower than the guideline value of As ($10\ \mu\text{g L}^{-1}$) established by the WHO for drinking water. The proposed method was successfully applied to determination of As in actual drinking water samples.

Achievements

Articles

1. Kenta Hagiwara, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “On-site determination of trace elemental ions in water using handheld X-ray fluorescence spectrometer”, *Advances in X-ray Chemical Analysis, Japan* 47 (2016) in press (in Japanese).
2. Kenta Hagiwara, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “On-site quantitation of arsenic in drinking water by disk solid-phase extraction/mobile X-ray fluorescence spectrometry”, *Talanta* 144 (2015) 788–792.
3. Yuya Koike, Kenta Hagiwara, “Determination of radionuclides in environmental samples using solid-phase extraction disk”, *Journal of the Society of Inorganic Materials, Japan* 22 (2015) 408–413 (in Japanese).
4. Kenta Hagiwara, Tetsuo Inui, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “Speciation of inorganic arsenic in drinking water by wavelength-dispersive X-ray fluorescence spectrometry after *in situ* preconcentration with miniature solid-phase extraction disks”, *Talanta* 134 (2015) 739–744.
5. Kenta Hagiwara, Tetsuo Inui, Yuya Koike, Toshihiro Nakamura, “Determination of diphenylarsinic acid, phenylarsonic acid and inorganic arsenic in drinking water by graphite-furnace atomic-absorption spectrometry after simultaneous separation and preconcentration with solid-phase extraction disks”, *Analytical Sciences* 29 (2013) 1153–1158.

Brochure

1. Kenta Hagiwara, Tetsuo Inui, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “Speciation of arsenic in drinking water”, *Prospect and Topics, 63th Annual Meeting of the Japan Society for Analytical Chemistry* (2014) 5 (in Japanese).

Award

1. Student encouragement award, *51th Discussion Meeting on X-ray Analysis* (2015).

Conference presentations

1. Kenta Hagiwara, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “*In situ* determination of arsenic in water by handheld X-ray fluorescence spectrometry”, *Pacifichem2015* (2015).
2. Kotaro Ochi, Yuichi Kurihara, Ryo Aobayashi, Kenta Hagiwara, Norio Nogawa, Toshihiro Nakamura, Yuya Koike, ”The activity concentrations of radiocesium in Tamagawa River Watershed, western district of Tokyo after the Fukushima Daiichi nuclear power plant accident”, *Pacifichem2015* (2015).
3. Kenta Hagiwara, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “On-site quantitation of toxic elements in water by handheld X-ray fluorescence spectrometry”, *51th Discussion Meeting on X-ray Analysis* (2015) (in Japanese).
4. Ryoken Shiobara, Kenta Hagiwara, Wataru Matsuda, Atsushi Ohbuchi, Toshihiro Nakamura, Yuya Koike, “A proposal of safety education using portable X-ray fluorescence spectrometer”, *51th Discussion Meeting on X-ray Analysis* (2015) (in Japanese).
5. Kenta Hagiwara, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “Speciation of selenium in water by disk solid-phase extraction/X-ray fluorescence spectrometry”, *64th Annual Meeting of the Japan Society for Analytical Chemistry* (2015) (in Japanese).
6. Daisuke Fukuda, Yuichi Kurihara, Ryoken Shiobara, Kenta Komatsubara, Kenta Hagiwara, Toshihiro Nakamura, Yuya Koike, “Separate determination of natural radionuclides in mineral using solid-phase extraction”, *64th Annual Meeting of the Japan Society for Analytical Chemistry* (2015) (in Japanese).
7. Kenta Hagiwara, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “On-site quantitation of arsenic in water by disk solid-phase extraction/handheld X-ray fluorescence spectrometry”, *75th Discussion Meeting on Analytical Chemistry* (2015) (in Japanese).
8. Wataru Matsuda, Yuichi Kurihara, Kenta Hagiwara, Yuki Iwahana, Tetsuo Inui, Atsushi Ohbuchi, Toshihiro Nakamura, Yuya koike, “Determination of ^{90}Sr in soil sample by solid-phase extraction disk”, *13th scientific congress of Japanese Society of Radiation Safety Management* (2014) (in Japanese).
9. Kenta Hagiwara, Tetsuo Inui, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, ”Screening for speciation of arsenic in water by disk solid-phase

extraction/X-ray fluorescence spectrometry”, *63th Annual Meeting of the Japan Society for Analytical Chemistry* (2014) (in Japanese).

10. Toshimitsu Araki, Tetsuo Inui, Kenta Hagiwara, Toshihiro Nakamura, “Determination of rare earth elements in vitrified rock by solid sampling graphite furnace atomic absorption spectrometry”, *63th Annual Meeting of the Japan Society for Analytical Chemistry* (2014) (in Japanese).
11. Kenta Hagiwara, Tetsuo Inui, Yuya Koike, Mamoru Aizawa, Toshihiro Nakamura, “Speciation of arsenic in water by solid-phase extraction/X-ray fluorescence spectrometry”, *74th Discussion Meeting on Analytical Chemistry* (2014) (in Japanese).
12. Kenta Hagiwara, Tetsuo Inui, Toshihiro Nakamura, “Determination of diphenylarsinic acid, phenylarsonic acid and inorganic arsenic in drinking water based on solid-phase extraction”, *ASIANALYSIS XII* (2013).
13. Kenta Hagiwara, Tetsuo Inui, Toshihiro Nakamura, “Separate determination of inorganic arsenic and phenylarsenic compounds in water using solid-phase extraction”, *73th Discussion Meeting on Analytical Chemistry* (2013) (in Japanese).
14. Kenta Hagiwara, Tetsuo Inui, Nao Kamakura, Toshihiro Nakamura, “Separate determination of As(III), As(V) and phenylarsonic acid in water by solid-phase extraction/atomic absorption spectrometry, version 2”, *61th Annual Meeting of the Japan Society for Analytical Chemistry* (2012) (in Japanese).
15. Kenta Hagiwara, Nao Kamakura, Tetsuo Inui, Toshihiro Nakamura, “Separate determination of As(III), As(V) and phenylarsonic acid in water by solid-phase extraction/atomic absorption spectrometry, version 1”, *72th Discussion Meeting on Analytical Chemistry* (2012) (in Japanese).

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Kenta Haginara

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